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IN THE
REALM OF CARBON

By H. G. DEMING

GENERAL CHEMISTRY

An interesting presentation of the subject of Chemistry, with everyday illustrations of abstract principles, numerous cuts, and photographs of industrial processes. Second Edition, Revised. Cloth; 5½ by 8½; 650 pages; 128 figures.

By H. G. DEMING

AND

SAUL B. ARENSON

EXERCISES IN GENERAL CHEMISTRY

By H. G. Deming and Saul B. Arenson, Assistant Professor of Chemical Engineering, University of Cincinnati. Second Edition, Revised. Cloth; 6 by 9; 282 pages; 28 figures.

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IN THE REALM OF CARBON

The Story of Organic Chemistry

BY

HORACE G. DEMING

*Professor of Chemistry, University of Nebraska
Recently in Charge of the Department of Information
of Arthur D. Little, Inc.*

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The end of our foundation is the knowledge
of causes, and secret motions of things; and
the enlarging of the bounds of human empire,
to the effecting of all things possible.

FRANCIS BACON

PREFACE

THIS book is intended for the general reader who would like to know something of the manner in which organic chemistry grew and developed, and something of its contributions to the comforts and conveniences of modern life. When supplemented by lectures in which general principles are treated more fully than has here been possible, it is also intended to serve as an introductory textbook of organic chemistry for students not specializing in chemistry. Too often the pleasure that such students might find in the subject is stifled by a useless burden of systematic detail.

The concluding chapters review the chemical activities of bacteria, plants and animals. Man's labored syntheses in test-tubes, retorts and beakers are placed in contrast with the swift elaboration of the most complex compounds, by living cells. Man seems but a bungling apprentice in the magic arts, when Nature, mistress of magic, shows what she can do.

The author's colleagues of Arthur D. Little, Inc., including E. C. Crocker, M. R. Eames, A. W. Francis, W. A. Gallup, W. F. Goldsmith, Wallace Murray, and Wm. H. Staebner read and criticized portions of the manuscript dealing with several of the applications of organic chemistry in industry. Suggestions were furnished by H. S. Mork with respect to the section on rayon; and by J. B. Crockett and A. J. Puschin with respect to that dealing with rubber. The sections dealing with plastic materials had the benefit of the criticism of men who are active in the development of the individual plastics there described, including J. M. DeBell, John D.

Moore, E. E. Novotny, Leon V. Quigley, A. O. Rayner, H. S. Spencer, R. L. Simmonds and A. S. Zimmermann. Professors H. H. Waite and L. F. Lindgren of the University of Nebraska offered many valuable suggestions in the chapters dealing with the chemical activities of bacteria. Dr. Emma Anderson assisted in the chapters dealing with the chemical activities of plants. Dr. Miles Breuer read and criticized the chapter on the chemical products of the ductless glands. To all of these friends and to a number of the author's students who assisted with the proofs most cordial thanks are due. A book covering so wide a range of topics would certainly have incurred many serious errors if this criticism had been unavailable.

Valuable general and detailed criticism of the book as a whole was furnished by Prof. Lyman C. Newell of Boston University and by Prof. Roscoe C. Abbott of the University of Nebraska. Miss Caroline Allen kindly served as a standard lay reader, and did much to improve the clarity of difficult passages. The author is very grateful for the assistance of his daughter Eleanor, who found time in the midst of busy school days to type a large portion of the manuscript. The full-page drawings bear witness to the artistic skill of Miss Phyllis Dorr and Miss Theresa Libby.

H. G. D.

Lincoln, Neb.,
Dec. 1, 1929.

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PART I

LAYING THE FOUNDATIONS

IN THE REALM OF CARBON

CHAPTER I

A DREAM REDREAMED

PRIMITIVE man very early learned that the properties of materials might sometimes be altered to his advantage.

The Early
Chemical Arts

While he still sought shelter from wet weather beneath overhanging cliffs, and contended with the wolf and bear for a refuge in caves, he learned that wood may be hardened by charring in the embers of a fire; that the skins of animals may be preserved by salt, and rendered pliable by tallow; that food is often improved in flavor by being boiled or roasted; and that vessels made of plastic clay become nearly as hard as stone, when strongly heated.

As civilization advanced, such transformations of materials became more and more numerous. In the Valley of the Nile, five thousand years ago, most of the useful materials that surround our lives today were known and used. Linen, silverware, copper, bronze, glass, many paints and enamels, and most of the raw products on our bills of fare were all familiar to Tutankhamun. In the restaurant of a modern hotel, one may count only some half dozen strictly modern materials: the tungsten and molybdenum of electric light bulbs, aluminum trays, a necklace of Bakelite beads worn by a lady, and garments of rayon, perhaps dyed with coal tar dyes. Our automobiles are lacquered with a modern material, cellulose nitrate, and are built of special steels; but steel of a sort

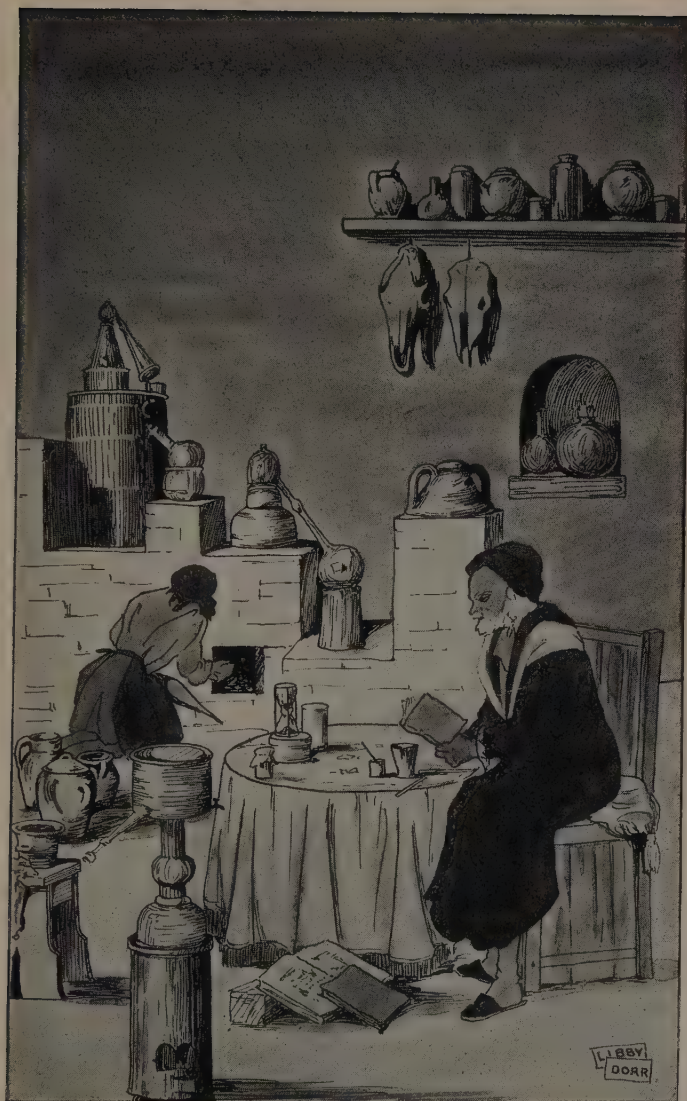
was manufactured in very ancient times, and even porcelain has been known for at least a thousand years.

Transformations of the raw materials of nature into new materials, of more useful properties, early led to the hope that man might transmute any material into any other, by divesting it of its familiar properties and substituting new ones. Surely he could convert all metals into gold—if he only knew how. Surely he could restore youth to the bodily organism, and prolong life indefinitely—if he only knew how. For a thousand years such results were believed to be possible, and other transformations of material things, without limit; and many workers claimed that their experiments had opened the way.

This was alchemy. Optimism passed all bounds. Men dreamed that the most unpromising raw materials might conceal unsuspected virtues; that gold would presently be created in abundance until everyone was rich; and that disease, misery, and old age were about to be forever banished from the earth. Only there was always a secret that must first be possessed. When the secret became a charm, the supernatural element crept in. It was commonly believed that the adepts of alchemy had bartered their souls in exchange for its dark and devious secrets.

True philosophers, during all these centuries, were honestly trying to advance man's ability to transform materials. As their exaggerated hopes failed to be realized, their dreams began to fade. Eventually they became confused with tricksters who sold charms and took advantage of men's credulity with the most brazen frauds. By Queen Elizabeth's time, alchemy was viewed with disfavor and ridicule, and several of the popes denounced it. It was magic, Black Magic, and the Church would have none of it.

After this, serious study was largely abandoned; men lost interest in the general problem of transforming materials, since the failure of alchemy to fulfill its promises



AN ALCHEMICAL LABORATORY

seemed to condemn it utterly. Nevertheless, there were some spirits in every age more hopeful than their fellows, who refused to relinquish a beautiful dream because of the hard facts of the laboratory. Even at the present day—in the midst of a thousand wonders brought forth by science—there exist multitudes of people whose manner of thought is still that of the Middle Ages, who are willing to believe whatever seems pleasant to believe. They are adepts in the gentle art of thinking wishfully. Thus alchemy still has its adherents. Until very recently an alchemical society existed, in which serious papers were read concerning the mystic Philosopher's Stone, or describing attempts to prepare the Elixir of Life; and in 1928 some German business men were defrauded of several million marks, by being induced to invest in an enterprise for transmuting mercury into gold.

Yet for all but the most credulous of mankind, alchemy long ago passed out of existence, along with astrology, palmistry, phrenology, and the belief in witchcraft. In the turmoil of emotions and exchange of ideas, when East met West in the Crusades, a new spirit of inquiry was spread abroad through all the civilized earth. It first appeared as an artistic achievement, in the Thirteenth Century. The great cathedrals of Europe expressed a creative impulse that was presently to find expression in the edifice of science. Then, in the Fourteenth and Fifteenth Centuries, painting and sculpture were transformed by new artistic viewpoints and an experimentally developed new technique. Finally, the new spirit produced the art of printing, and thus found the means to perpetuate itself in the generations that were to come. The fall of Constantinople at that moment brought refugees into the West, with classical manuscripts that were forthwith printed; and the discovery of the New World stirred the imaginations of men.

At the beginning of the Seventeenth Century, inquisitive intelligence and its tool, the experimental method,

were already justified by the great advances they had produced in art, invention, exploration, and the diffusion of knowledge. The world was waiting for a stimulating expression of the methods and ideals of the new mode of thought. This came from Sir Francis Bacon, who was born in 1561, in the early part of the reign of Elizabeth and who, for a brief time, held the office of Lord Chancellor of England, under her successor. His service (*Novum Organum*, 1620) was to point out certain shortcomings of undirected thought and haphazard inference, certain frailties of the human intellect that impede us in our search for truth.

Yet not content with pointing out the pitfalls awaiting the unguided and unguarded intellect, Bacon illustrated some principles that would enable reason to proceed more securely and more confidently in its quest of truth. He was not himself a contributor to experimental science. His part was to point out the way. He summoned all thinking men to give heed to a plan of procedure—the scientific method—that disclosed new worlds and promised new conquests on all the frontiers of knowledge.

Immediately, noteworthy advances were made in anatomy, physiology, astronomy, and the physical sciences.

Robert Boyle The problem that had engrossed the alchemists made progress, too, when an Irishman named Robert Boyle, in his treatise "The Skeptical Chymist," formulated a theory regarding the transformations of material things, which replaced magic by science, and became the guiding principle of the chemistry of later days. Boyle recognized that the properties of materials are not mere accidental coverings wrapped about an inner core of reality. One cannot by any process divest lead of its properties, and endow it with the properties of gold, as one might change a suit of clothes. On the contrary, our universe is composed of a limited number of elements which are not transformable into each other by chemical procedures, though they may enter into union with each

other to produce new materials, from which the constituent elements may again be separated with all their original properties.

Accordingly, if it is found possible to transform a given material into another, it is only because the first contains all the elements that are necessary to the making of the second. If a reddish earth can be transformed into iron, it is only because it contains iron in combination with something else, which for the moment disguises that metal. No material was ever produced from others unless its constituent elements were all hidden away in the latter, from the beginning.

Thus alchemy perished, and in its place arose chemistry. Its first problem was to determine what the elements

are of which the universe is composed, and what the means are by which they can be brought into combination with one another

or separated from one another. Joseph Black, in England, in 1755, made the first quantitative studies of chemical changes; that is, the first studies in which the materials taking part in those changes were accurately weighed or measured. Next, Sweden contributed the work of the great experimentalist, Scheele, who discovered oxygen, chlorine, nitrous oxide, hydrogen sulfide, and many other important substances. Oxygen, indeed, was discovered independently by Scheele in Sweden, Priestley in England, and Lomonosoff, in Russia.

Some of the most familiar of the chemical changes of everyday life, such as respiration, combustion, rusting, and decay, have to do with oxygen. Accordingly, a long stride was taken toward establishing chemistry as a science when the French chemist Lavoisier, in 1777, compelled the acceptance of a general explanation that showed that these four types of chemical change—respiration, combustion, rusting and decay—are all processes of union with oxygen. This achievement, and his demonstration of the importance of accurate weighing, as a means for establishing the laws of chemical change, made

**The Beginnings
of Chemistry**

Lavoisier the leader of the group of men who founded modern chemical science.

Now that the way was shown, chemistry made rapid progress. Oxygen turned out to be the most plentiful element. Lavoisier made it the center of his chemical system. Element after element was added to the list. Berzelius, a great Swedish chemist, whose work immediately followed that of Lavoisier, had five new elements to his credit. Sir Humphry Davy, an English chemist, in 1807 and 1808 discovered six—a greater number than stands to the credit of any other discoverer. Thousands of minerals in all parts of the world, the ocean and the atmosphere were so thoroughly ransacked, that by 1830, fifty years after the early work of Lavoisier, fifty-three elements had been discovered, out of the ninety known today. In fact, not one element has been found in the hundred years that have since elapsed that is present in more than traces in the earth's crust and atmosphere, if we except fluorine and argon. Fluorine remained unisolated in elementary form until 1886, because it is chemically so very active; while argon was overlooked until 1894 because it is totally inactive.

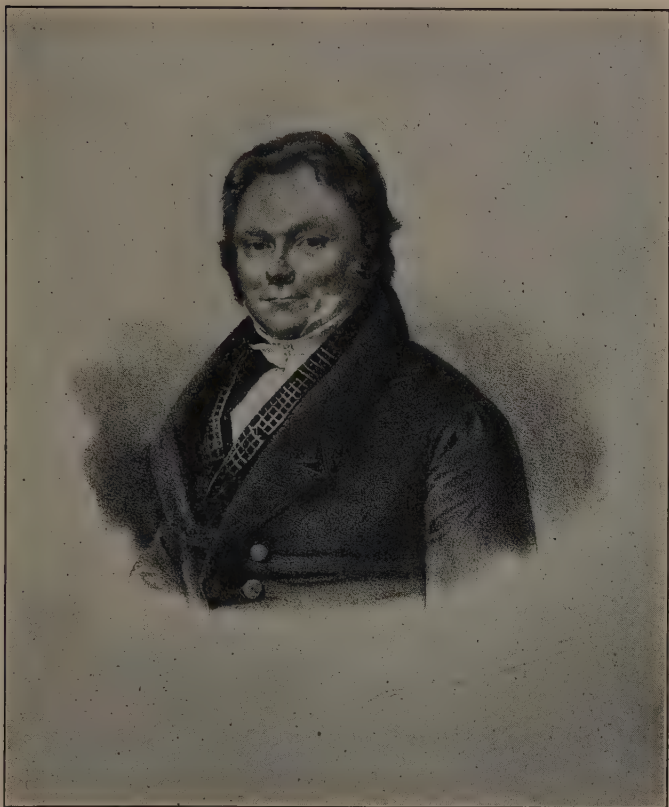
With the discovery of new elements came the development of means for their detection and separation from each other. Berzelius himself was one of the leaders here. By 1830 methods of analysis were worked out, similar to those that are in use today. Then as now you might send a well-qualified chemist almost anything, from a handful of earth to a rare mineral, and get an accurate statement of the proportions of the different elements contained in it.

While the rocks and minerals of the earth's crust were being eagerly examined for new elements, a beginning was also made in the study of the compounds (presently called *organic compounds*) produced by living plants and animals. Lavoisier himself showed that the living uni-

verse, in its infinite variety of form and function, displays no such number of elements as the non-living universe of earth, ocean and atmosphere. The living plants and animals, from the largest mammals to microscopic bacteria, are alike composed of compounds of the element carbon, usually in combination with the elements hydrogen, oxygen, nitrogen, phosphorus, and often small amounts of a few other elements. The living universe, then, is a universe of carbon. Carbon is the one touch of nature that makes the whole world kin. So far as anyone could see in the days of Lavoisier, or may guess now, the processes of plants and animals would still go on as before if many of the most important metals, and even some familiar non-metals, were suddenly to pass out of existence.

For a time it was thought that the compounds of the organic world were created by the action of a "vital force" peculiar to living organisms. The chemist, who had learned how to produce inorganic acids, bases and salts of all kinds, by simple reactions in test-tubes and beakers, was overcome with a sense of helplessness and awe at the threshold of the organic realm. Then, one by one, some of the simplest organic compounds (urea, acetic acid, benzene and a number of alcohols and organic acids) were synthesized—that is, produced by combining simpler compounds or perhaps by combining elements. About 1860 some important dyes, until then obtained only from the indigo and madder plants, were built up step by step from simpler compounds derived from coal tar. At present nearly all the types of organic compounds that are found in living plants and animals have been produced in the chemist's laboratory, and in addition, thousands of others quite unknown in nature. Today organic chemistry is simply the chemistry of the compounds of carbon, without regard to their origin.

Now again optimism is at its height. We hear on



Courtesy of Rudolf Lesch

JÖNS JACOB BERZELIUS

b. Väfersunda, Sweden, 1779. Studied medicine at Stockholm. He did much to develop the methods by which the composition of mineral substances is still determined, and discovered five elements: cerium, thorium, zirconium, selenium and silicon. He made the first reasonably accurate analyses of organic compounds, invented the chemical symbols used today, and derived the first formulas of organic compounds. He devoted ten years to the accurate determination of atomic weights, and many of his results have only been slightly improved by later workers. *d.* Stockholm, 1848.

every hand that chemistry has outrun nature. Coal tar has been converted into medicines, and **White Magic** into dyestuffs of a thousand hues. Lemon grass is transformed into violet perfume, starch into rubber, sawdust into sugar, cotton linters into explosives, lacquers, and rayon. Chemical enthusiasts inform the public that the world may presently cease growing corn and potatoes, because compact and easily digested substitutes are going to be created, which will make our present bills of fare seem as primitive as the diet of roots and insects on which our ancestors lived before the dawn of civilization. The quiet life of field and countryside is about to be superseded by syntheses in chemical factories. The future promises to say it with test-tube and retort instead of with flowers.

With each new advance in the synthesis of medicines someone is heard to announce the dawning of a new age, in which all human ills are to be overcome by the triumphs of the laboratory. Chemical progress is advertised as being about to free the human race from most of its physical defects and frailties. Imagination puts no limits to the triumphs of synthesis in the immediate future. The dream of alchemy is being redreamed. It is magic again, though White Magic this time—magic purely beneficent in its purposes, developed without resort to secret understandings with the Powers of Darkness.

Is this dream to be realized? Has chemical progress really outrun nature? Have the test-tube and retort really won such significant victories? How far has synthesis in the laboratory actually advanced in comparison with synthesis by living cells? Just where do we stand? This book seeks the answer.

CHAPTER II

ATOMS AND MOLECULES

WHEN chemists first attempted to unscramble the universe into its constituent elements, they were influenced by all that had been thought and written in the centuries gone before. Alchemists, philosophers, churchmen, and mystics—the voices were confused and contradictory. Where so many divergent opinions were held regarding the nature of the universe, most of them had to be wrong. Yet when many earnest seekers are groping through darkness toward the truth someone may actually lay hands upon it. It happened that among all the suggestions that came down from the past, one stood the test of experiment and is today well established. Thus we are introduced to atoms and molecules—the universe of the infinitely small, beyond the reach of microscope. Happenings in this universe determine those of our own.

To the observer of nature as to the student of history there sometimes comes a solemn sense of the changeableness of material things. Our friends and companions present altered aspects to us and we to them, as days go by. Glittering novelties become battered heirlooms.

**A Suggestion
from the
Ancient Greeks**

The gay raiment of a royal court fades to the moth-eaten relics of a museum. Solid steel, fit to endure for centuries, in the end falls victim to rust and corrosion. The very mountains are worn away to level plains during the lapse of ages, and the bottom of the ocean is elevated mountain high. When we contemplate the apparent course of stellar evolution we can foresee that our sun, with its accompanying planets, may go wheeling on

through eons of continued change long after the human race shall have passed away.

So, in the long-vanished days of Ancient Greece—days that once seemed vivid and eventful—men paused to consider the mystery of never-ceasing change. Was there nothing in all the wide world quite fit to withstand the onslaughts of time? Behind the ever-shifting veil of the temporal was there nothing eternal?

Some hint of an answer may have come from the observation that creation, from age to age, presents an ever-changing face, yet does not utterly pass away. "The universe is seen to remain undiminished, inasmuch as all bodies that depart from anything lessen that from which they pass, and bless with increase that to which they have come." In brief, the fact that the universe alters its appearance but does not pass away was assumed, by Democritus and others as far back as B.C. 430, to be due to its being composed of minute particles (*atoms*) so solidly constructed as to endure forever. The manifold changes of the visible world, then, are effected by breaking down material things into the different kinds of atoms that compose them, and rearranging these atoms into new structures, much as one might demolish a building and use the individual bricks to construct another.

Of the writings of Democritus himself we have no more than fragments. Yet his ideas became a part of the philosophy of the Epicureans, preserved
Lucretius in the resplendent imagery of the Roman poet Lucretius, a contemporary of Cicero and Cæsar. The atoms were all presumed to be *so small as to be invisible*. Lucretius writes: "As the sun's year rolls round again and again, the ring on the finger is worn thin, the fall of dropping water hollows the stone, the bent iron plowshare imperceptibly grows smaller in the fields, we see the paved stone streets worn away by the feet of the multitude, and the brazen statues near the gates show their right hands made smaller by the touch of the throngs

who greet them and pass by. All these things, then, we see to be diminishing, as they are worn away; yet what particles leave them on each occasion, jealous Nature has prevented us from seeing. Lastly, whatever time and nature add little by little to things, impelling them to grow larger, the straining sight of the eye can never behold, nor what is lost when things grow old, through time and decay. Nor can you perceive what the rocks, which overhang the sea, and are eaten away by the corroding salt of the ocean, lose every time they are washed by the waves. Thus Nature carries on her operations by unseen particles."

The most important assumption about the atoms, however, was that *they remain undivided in all the manifold transformations of material things*. "From them Nature, keeping safe the seeds of things, suffers not anything to be torn away, nor ever to be removed."

If we think of the universe as being composed of atoms, the question at once arises whether there is an infinite number of different kinds of atoms, corresponding to the almost endless variety of material things, or whether all material things are composed of a relatively few different kinds of atoms. The modern view is that advanced by Dalton, an English schoolmaster, in 1808, that there are only as many chemically different kinds of atoms as there are different elements—as we now know, only about ninety. The thousands of more complex materials, according to this view, are constructed from these ninety sorts of atoms, by bringing them into special groupings or arrangements, each characteristic of a given material. Such groupings, sets or clusters of atoms came to be called *molecules*. We think of the properties of matter in bulk as being determined by the nature of its molecules. Sugar is sweet, soluble in water, of a definite crystalline form, and readily decomposed by heat because its molecules are of such a nature as to give it these properties.

If this view is correct, then to convert any given material into another one must remodel its molecules. The atoms within each molecule of the original material must be brought into new groupings or new arrangements. The problem of chemistry of transforming materials becomes therefore the problem of transforming molecules.

Whether a material exists in a gaseous, liquid or solid state is determined by the arrangement of its molecules.

**The Three
States of
Matter**

If these are relatively far apart we have a gas, if relatively close together a liquid, and if regularly spaced or arranged with respect to each other, a solid. By analogy, a scattered group of people upon the street would represent a gas; a dense crowd in the subway, a liquid; and an audience in a theatre, a solid; for in these illustrations we have respectively relatively distant, relatively close, and ordered spacing.

Of the three states of matter the gaseous would seem to be the most unpromising as an object of study, for gases are elusive, intangible materials that require special apparatus to contain them. Also, most gases are invisible. Nevertheless, they have the advantage of being physically much alike. All gases, for example, are nearly equally compressible, nearly equally expansible by heat, and absorb nearly equal quantities of heat per unit volume when they are heated through a given temperature range. Moreover, many of the simplest substances known are gases, whose composition had to be worked out before chemistry could progress very far. Thus gases and their properties occupied a prominent place in the early history of the science.

The distinction just made between the three states of matter, based on the spacing of molecules, was recognized in the time of Newton, over two hundred years ago. In 1738 Daniel Bernouilli elaborated the thought that the molecules of a gas or vapor are not only far apart, but

**Gases in
Detail**

are in rapid motion in all directions, and thus rain down blows on the walls of the containing vessel—such a continual succession of blows that they seem to exert a constant pressure. If a gas is heated it exerts more pressure, presumably because the molecules move more rapidly and thus deal harder blows against the walls.

The English physicist, James Maxwell, who laid the foundations of much of our present knowledge of light and electricity, brought in the assistance of mathematics at this point, and showed that we can calculate the speed of gas molecules from the pressure which their blows deliver against the walls of the vessel. We do not need to know the number of molecules, nor how much they individually weigh, but only the total mass of gas confined in a given volume. It turns out that a molecule of hydrogen, the lightest known molecule, has on the average at room temperature a velocity of about one mile a second.

Heavier molecules move more slowly. Nevertheless all molecules, of whatever sort, possess the same energy of motion at a given temperature, for the extra mass of the heavier ones makes up for their slower speed. An important consequence of this is that all molecules, of whatever sort, beat back their neighbors to an average distance which depends on the temperature, but which is the same for all gases. In other words, *under like conditions*, all gases have the same average space between molecules; or, *equal volumes of all gases contain equal numbers of molecules*. This is the *Principle of Avogadro*, first stated in 1811, but delayed for nearly fifty years in its general application, until its usefulness was pointed out by an Italian chemist, Cannizzaro, in 1858.

A given vessel, at a given temperature and pressure, will contain the same number of molecules of ammonia, nitrogen, carbon dioxide, or any other gas. As we have said, heating makes the molecules move faster, deal each other harder blows, and drive each other farther apart.

At higher temperature, therefore, a smaller number of molecules of gas is contained within the vessel. Compression, on the contrary, forces the molecules closer together, and allows more of them to be contained in the vessel. Still, at any specified temperature and pressure, the number of molecules of gas that a vessel will contain is the same for all gases.

Equal numbers of molecules in equal volumes of all gases! Here is an astounding fact, which had a tremendous effect on the development of chemistry when it had once been recognized, for it provided a means for determining relative weights of molecules simply by comparing weights of equal volumes of gases. For example, if we find that carbon dioxide gas is about one-third heavier than the same volume of oxygen gas, we know at once that a molecule of carbon dioxide is about a third heavier than a molecule of oxygen. Relative weights of molecules (now called *molecular weights*) have thus been determined for hundreds of different gases and vapors.

Oxygen is made the standard of comparison in finding relative weights of atoms and molecules, since it can be made to combine with nearly all other elements. A molecule of oxygen was arbitrarily taken as thirty-two units of weight, in order to make the lightest known particle (an atom of hydrogen) come out with a weight very nearly equal to one. Substances like cane sugar, which are not gaseous and not readily gasifiable, may still be soluble, in which case other methods have been found for obtaining their molecular weights.

Some important approximate molecular weights:

Oxygen.....	32	Ammonia.....	17
Hydrogen.....	2	Water vapor.....	18
Nitrogen.....	28	Chloroform vapor....	119.5
Carbon dioxide.....	44	Cane sugar.....	342

Today we not only know the relative weights of mole-

cules but even the relative weights of the atoms that compose molecules. Such relative weights of atoms are commonly called *atomic weights*.

The principle is simple enough: We survey all the compounds containing a given element such as chlorine, and take note of their molecular weights. Knowing the percentage of chlorine in each compound we may then compute the weight of chlorine in each molecular weight. The least weight of chlorine in the molecular weight of any chlorine compound is presumably due to a single atom of chlorine, and is accordingly the atomic weight of chlorine. Similarly the least weight of carbon found in a molecular weight of any compound of carbon is the atomic weight of carbon. By analogy, we may discover the weight of a sack of flour by taking note of the least weight of flour which a grocer ever delivers to any of his customers. By such methods as this the atomic weights of nearly all the elements have been determined.

Some common approximate atomic weights:

Oxygen.....	16	Chlorine.....	35.5
Hydrogen.....	1	Carbon.....	12
Nitrogen.....	14	Sulfur.....	32

Atomic weights range all the way from 1.008, which is the atomic weight of hydrogen, to 238.2, which is that of uranium. We note that the atomic weights of oxygen, hydrogen and nitrogen are just half their respective molecular weights. Thus a molecule of each of these gases contains two atoms, whence the formulas O_2 , H_2 , and N_2 , which are used to represent these elements in their ordinary gaseous condition.

Of course the molecular and atomic weights just discussed are merely relative figures, made in comparison with a molecule of oxygen taken as 32 units. If we could deal with atoms and molecules individually, how large would they be and how much would they weigh?

This question remained unanswered until the Twen-

Actual
Weights
of Atoms and
Molecules

tieth Century. Indeed, as late as 1910 chemical textbooks sometimes took the stand that atoms and molecules were perhaps after all mere creations of the human intellect, with no counterpart in nature, and that the atomic and molecular theories were only convenient frameworks on which to hang our odds and ends of information. Recent progress has changed all this. Calculations based on such diverse phenomena as the rate of wandering and manner of scattering of microscopic particles, the motion of electrified droplets in an electromagnetic field, the rate at which helium gas is produced from radium salts, and even the blue color of the sky, all agree in stating that you may find the actual weight in grams of any atom or molecule by dividing its relative weight by 6×10^{23} .*

The fact that such diverse phenomena all lead to the same result for the divisor to be used in finding the weight of an individual atom or molecule, is taken to be conclusive evidence of the actual existence of atoms and molecules. "In the mouths of three witnesses shall everything be established." To the chemist of today the individual atoms and molecules with which he deals are real—more real perhaps than the individual human beings that he meets on the streets. To most of us, no doubt, the best test of reality is self-consistency. The chemist believes in the actual existence of atoms and molecules because all the results of chemical research by thousands of investigators over more than a century find a convenient explanation in terms of them, and because no single fact has yet been discovered that would seem to call for a different interpretation.

It is true that some of the views that were held a century ago have had to be abandoned. Modern science,

* This means a "6" followed by 23 zeros, namely six hundred thousand million million million. It is called Avogadro's *number*, in honor of the man who, a century ago, first showed how the relative weights of molecules may be determined.

within the last few years, has come into possession of forms of energy incomparably more intense than those that were known even a generation ago. Thus the very atoms, in a few instances, have been disrupted. To ordinary chemical agencies, however, an atom is still an indivisible thing, so solidly constructed as to endure forever. In ordinary chemical reactions, atoms are merely rearranged into new groupings, with respect to one another, but are never subdivided.

The sizes of the atoms and molecules of some familiar gases have been estimated from the rate of passage of gases through capillary tubes. It turns out that about sixty million molecules of air may be laid down side by side in a distance of one inch. In a cubic centimeter of air—that is, a very small thimbleful—there are 27×10^{18} molecules—in other words, twenty-seven million million million. If this thimbleful of air were divided equally among all the inhabitants of the world, and molecules valued at a million for a cent, one's own individual share would be worth about ninety dollars. Again, an average-sized drop of water contains about 15×10^{20} molecules. If each molecule were a bullet, one drop of water would have supplied ten thousand million machine guns, firing 150 shots a minute, from the time of Cæsar to the present moment.

The impressive achievements of modern chemistry are based upon a suggestion from the Ancient Greeks. This assumes that matter is composed of minute particles called atoms—as many chemically different kinds of atoms as there are different elements, namely ninety in all. The transformations of one kind of matter into another, that are the chief concern of chemistry, are accomplished by combining and recombining atoms into groups, clusters, or assemblages of

**Small Sizes
and Large
Numbers**

Summary

atoms called molecules. In the gaseous, liquid, and solid states of matter the molecules are respectively widely scattered, closely packed, and regularly spaced with respect to one another.

Relative weights of molecules of gases (molecular weights) are determined by comparing weights of equal volumes. Relative weights of atoms (atomic weights) are determined by noting the least weight of each element that is contained in a molecular weight of any of the compounds of that element. The actual weight in grams of any atom or molecule may be found by dividing its relative weight by 6×10^{23} .

CHAPTER III

STOCK-TAKING WITHIN MOLECULES

TO TRANSFORM a given material into another, it becomes obvious that the molecules of both must be examined in detail. The problem is one of stock-taking within molecules. What elements and how many atoms of each are contained in a molecule of water, or in a molecule of cane sugar? The same question arises for thousands of other materials. If the answer can be determined, the chemist may hope to proceed in a systematic way, adding atom to atom, to construct a new type of molecule and thus produce a new material, with almost the ease and assurance with which a mason lays up bricks in a wall. This gives a definite practical interest to the question of the manner in which molecules are constructed.

A New Problem

Serious thought had to be devoted to this problem, and fifty years of labor on the part of many chemists before the solution was made clear. Because the molecules were too small to be dealt with individually, conclusions about them had to be inferred from a study of matter in bulk. We can best make this clear by imagining for the moment that automobiles were too small to be examined individually, but that we had access to statistics of a factory, which showed that for each million steering wheels built into its product, six million spark plugs were needed, four million wheels, and two million headlights. We might then conclude that each car possessed one steering wheel, six spark plugs, four wheels, and two headlights, or some multiples of these numbers. So, by analyzing a visible and

weighable amount of cane sugar, some conclusions may be drawn concerning the relative numbers of atoms of carbon, hydrogen and oxygen in one molecule of it; and similarly for other materials of definite composition.

How then is the chemical composition of matter in bulk to be determined? How may we know what ele-

**Chemical
Analysis**

ments and what proportion of each go into the making of familiar materials? It depends on the nature of the materials themselves. There are a few materials which, when heated, decompose directly into their constituent elements. If we heat a sample of silver oxide it is decomposed, losing oxygen, and leaving behind metallic silver. By weighing this in comparison with the weight of the original sample, we may find the percentage of silver in silver oxide.

Sometimes a material may be decomposed by an electric current. A sample of a copper salt, for example, may be dissolved in water and all the copper plated out by an electric current as metallic copper, on a weighed sheet of platinum foil. The increase in weight of the foil gives the weight and percentage of copper in the original salt.

Nevertheless, the materials of the organic universe—the compounds of carbon—are not decomposable by any such simple means. If you heat a sample of sugar it is decomposed, to be sure, but into a complicated mixture of products rather than into its constituent elements, carbon, hydrogen and oxygen. A special method therefore had to be developed for determining the composition of organic compounds. In principle, it consists in burning the compound and determining the weights of water and carbon dioxide that are produced. Our knowledge of the percentage of carbon and hydrogen in organic compounds thus depends on an accurate knowledge of the composition of water and carbon dioxide, since the water produced in burning a compound measures the hydro-

gen, and the carbon dioxide measures the carbon that the compound contains.

In 1781 the English chemist Cavendish observed that when a mixture of hydrogen and oxygen gases is exploded by an electric spark, the result is water. He noted that about twice as great a volume of hydrogen is needed as of oxygen. Then, in 1801, two other Englishmen, Nicholson and Carlisle, decomposed water by passing an electric current through it, and again obtained two volumes of hydrogen for every volume of oxygen. This experiment, the first example of a chemical change induced by an electric current, was the forerunner of the great electrochemical industries of today.

Composition of Water

Oxygen was known to be about sixteen times as heavy as hydrogen, or eight times as heavy as twice its volume of hydrogen. Thus it was plain that water consists of about eight parts of oxygen and one part of hydrogen by weight. It was necessary to determine this ratio with the greatest care, since it was to be made the basis of calculation of the percentage of hydrogen, and consequently the basis for the chemical formula of every one of the great host of organic compounds. The Swedish chemist Berzelius was one of the first to attempt this. Then the French chemist Dumas, in 1842, repeated the work with the most elaborate precautions, devoting months to the task. Some fifty years later two American chemists, Edward Morley and William A. Noyes, separately made many other determinations, by other methods still. The work of Morley was continued during more than twelve years.

The more painstakingly such experiments were carried through, the more closely they agreed with each other. It was made very plain that no matter by what method water is produced, the proportion of hydrogen and oxygen it contains is constant. The accepted present figures, based on the work of Morley and of Noyes, are

8 parts of oxygen to 1.008 parts of hydrogen. Otherwise expressed, water contains 88.81 per cent oxygen and 11.19 per cent hydrogen by weight.

The composition of carbon dioxide was also the object of careful investigation during more than a century. In principle the task was easy. A known weight of pure carbon was burned, producing carbon dioxide gas, which was absorbed in some material whose increase in weight was noted. The amount of this increase was the weight of the carbon dioxide produced from the given weight of carbon. In practice innumerable difficulties were met. First there were difficulties in the preparation of pure carbon. Many investigators burned samples of diamond as the purest form of carbon obtainable in nature. Then something had to be found that would completely absorb the carbon dioxide produced in the burning without absorbing or losing anything else. The final result of most accurate recent determinations is that carbon dioxide contains 27.28 per cent carbon and 72.72 per cent oxygen.

These careful determinations of the percentage composition of water and carbon dioxide were only an incident to the development of a method for determining the composition of organic compounds, now called *analysis by combustion*. Lavoisier burned samples of wax, alcohol or other organic materials in a current of air, and collected the carbon dioxide and water vapor that were formed, using an apparatus shown in the sketch on p. 28. Yet many organic substances fail to burn completely under such conditions, and the water and carbon dioxide were not completely absorbed in the apparatus of Lavoisier. Berzelius developed a very different type of apparatus, shown in the second sketch on page 28, with which he obtained such accurate results that many of the formulas

he derived for organic compounds are accepted today, after more than a century.

The German chemist Liebig, as an incident to a series of researches in organic chemistry lasting over twelve years, perfected a more accurate method still. In recent and present-day chemical laboratories Liebig's charcoal furnace has been replaced by a gas or electric furnace; a current of pure oxygen is now led into the apparatus from a cylinder of compressed oxygen, and still other details have been improved. Yet in principle the method of analysis by combustion remains as Liebig perfected it. It enables the percentage composition of organic compounds to be determined with such precision that it is rare indeed that an organic formula needs to be revised by so much as a single atom of hydrogen.

Now let us apply Liebig's method to an actual case. We burn a sample of alcohol weighing one gram, and absorb and weigh the water vapor and carbon dioxide that are formed. We obtain 1.1737 grams of water vapor, which we know contains 11.19 per cent of hydrogen; and 1.9110 grams of carbon dioxide, which we know contains 27.28 per cent of carbon. Thus the sample of alcohol must have contained:

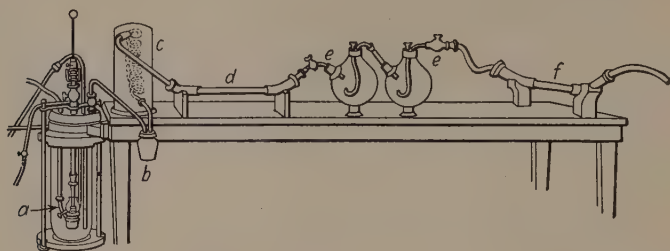
Finding the
Weight of
Each Element
in a Molecule

$$\begin{aligned} 11.19\% \times 1.1737 &= 0.1313 \text{ gram of hydrogen;} \\ 27.28\% \times 1.9110 &= 0.5213 \text{ gram of carbon.} \end{aligned}$$

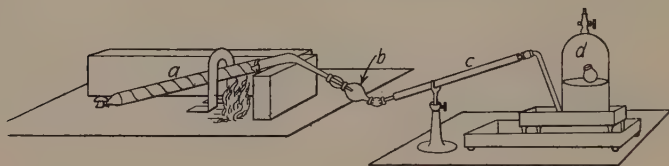
But since the sample weighed one gram it must have contained 13.13 per cent hydrogen and 52.13 per cent carbon. There remains 34.74 per cent, which is assumed to be oxygen, in the absence of proof that any other element is present. If the compound contained sulfur, chlorine, nitrogen or other elements, these would of course need to be determined also, by special methods that we need not pause to describe.

When we have once found the percentage of each ele-

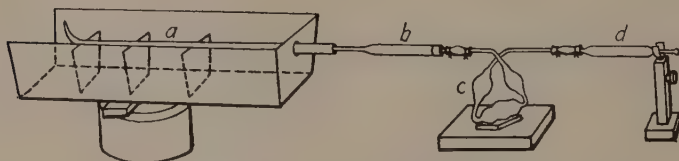
THE EVOLUTION OF ANALYSIS BY COMBUSTION



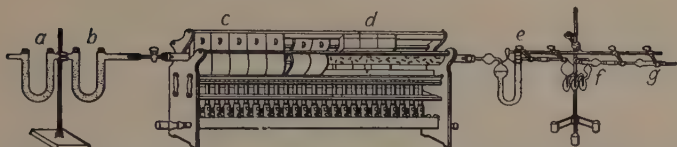
LAVOISIER, 1784. *a*, lamp in which the sample was burned in a current of air; *b*, small flask in which most of the water produced was collected; *c*, coiled condenser; *d*, tube filled with calcium chloride to absorb any water that failed to be condensed; *e, e*, two to six vessels containing a solution of caustic potash to absorb carbon dioxide; *f*, tube containing calcium chloride to absorb moisture lost by caustic potash solution. Joints of this apparatus were sealed with clay.



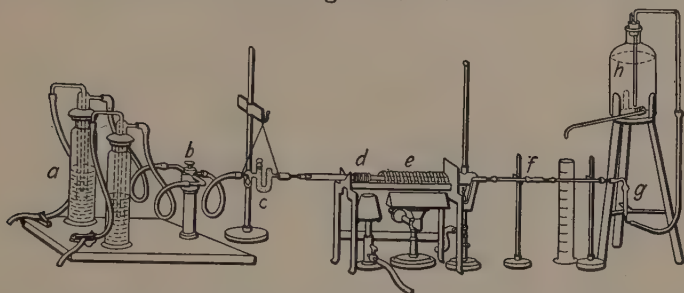
BERZELIUS, 1815. *a*, glass tube wrapped in tin foil. This contained the sample, mixed with potassium chlorate (to furnish oxygen) and common salt. A charcoal fire was lighted next the brick, and the sample slowly heated by moving the horse-shoe shaped iron screen toward the left. *b*, receiver in which most of the water condensed; *c*, tube containing calcium chloride; *d*, bulb floating in mercury, and containing solid caustic potash, which slowly absorbed the carbon dioxide. The connections in this apparatus were of homemade rubber tubing, tied with silk.



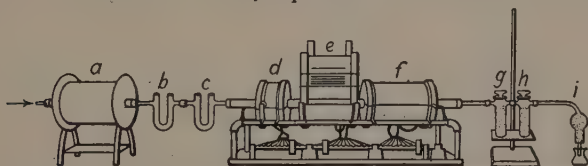
LIEBIG, 1831. *a*, hard glass tube heated in a bed of glowing charcoal, and containing the sample, mixed with copper oxide (to furnish oxygen); *b*, tube containing calcium chloride; *c*, bulb or several bulbs containing caustic potash solution; *d*, guard tube containing calcium chloride.



GAS-FIRED FURNACE, 1900. *a*, tube containing soda-lime to remove carbon dioxide from incoming current of oxygen or air; *b*, tube containing calcium chloride; *c*, portion of furnace containing sample, sometimes mixed with finely divided copper oxide; *d*, portion of furnace containing granular copper oxide, heated to redness from the beginning; *e*, tube containing calcium chloride; *f*, bulbs containing caustic potash solution; *g*, guard tube containing calcium chloride.



MICRO-COMBUSTION APPARATUS (Pregl), 1924. For combustion of very small samples. *a*, pressure regulator for oxygen inlet; *b*, three-way cock for changing from air current to oxygen current; *c*, U-tube containing soda lime and calcium chloride; *d*, end of combustion tube containing sample; *e*, combustion tube containing a mixture of copper oxide and lead chromate (to furnish oxygen), lead peroxide (to retain sulfur) and silver wool (to retain halogens); *f*, absorption tubes containing calcium chloride and soda lime; *g*, guard tube containing calcium chloride; *h*, aspirator.



MODERN APPARATUS (Harry L. Fisher), 1927. *a*, electric furnace containing a coil of copper oxide to oxidize impurities in the incoming current of oxygen; *b*, tube containing soda-lime; *c*, tube containing calcium chloride; *d, e, f*, electric furnace in which the sample is burned. The left-hand section, *d*, contains a roll of copper oxide gauze; the middle section, *e*, a porcelain or platinum boat, holding the sample; the right-hand section *f*, copper oxide and cerium dioxide; *g*, bottle containing calcium chloride or a mixture of hygroscopic alumina and pumice; *h*, bottle containing a mixture of caustic soda and asbestos; *i*, guard tube containing calcium chloride, with a tip dipping into palladium chloride solution, which darkens if unburned carbon monoxide escapes.

ment in an organic compound by the method just described, it is very easy to determine how many atoms of each element there are in a molecule of the compound. Let us illustrate with alcohol. Alcohol vapor is nearly fifty per cent heavier than an equal volume of oxygen gas, hence its molecular weight is nearly 50 per cent greater than 32, that is, roughly 46. Alcohol contains 52.13 per cent carbon, 13.13 per cent hydrogen, and 34.74 per cent oxygen. The total weight of each element in the molecular weight of alcohol is therefore:

$$\begin{aligned} 52.13\% \times 46 &= 24 \text{ parts of carbon;} \\ 13.13\% \times 46 &= 6^+ \text{ parts of hydrogen;} \\ 34.74\% \times 46 &= 16 \text{ parts of oxygen.} \end{aligned}$$

If we compare these figures with the respective atomic weights ($C=12$, $H=1.008$, $O=16$), we see that there are two atoms of carbon, six atoms of hydrogen, and one atom of oxygen in a molecule of alcohol. Alcohol is therefore represented by the formula C_2H_6O . By analogy a grocer may discover how many packages of each commodity he has in stock by dividing the total weight of each by the weight of a single package.

As another example, let us consider chloroform. Its molecular weight (determined by comparing the weight of chloroform vapor with the weight of an equal volume of oxygen gas) is roughly 119.5. An analysis by combustion shows that chloroform contains about 10.05 per cent carbon, 0.85 per cent hydrogen, and 89.10 per cent chlorine. The total weight of each element in the molecule is therefore:

$$\begin{aligned} 10.05\% \times 119.5 &= 12 \text{ parts of carbon;} \\ 0.85\% \times 119.5 &= 1^+ \text{ part of hydrogen;} \\ 89.10\% \times 119.5 &= 106.5 \text{ parts of chlorine.} \end{aligned}$$

If we compare these weights with the atomic weights of these elements ($C=12$, $H=1.008$, $Cl=35.5$) it is plain that a molecule of chloroform contains one atom of carbon, one atom of hydrogen and three atoms of chlo-

rine. Chloroform is therefore commonly represented by the formula CHCl_3 . We see that a chemical formula is intended to express how many atoms of each kind there are in a molecule of the compound.

We have cut straight to the heart of the mystery of how chemical formulas are derived. It may have made dull reading, but we could not escape that if we were to deal with the question at all.

Chemical Formulas

Now let us summarize: (1) To take stock of the numbers of atoms of each kind within a molecule, we must determine the percentage of each element in the given substance. If it is a compound of carbon, this usually means that we must burn it, and take note of the weights of carbon dioxide and water produced. Thus we arrive at what is called the *percentage composition* of the substance. (2) If we know the molecular weight, we then calculate the total relative weight of each element in the molecule. (3) Finally, by comparing these total relative weights with the relative weights of individual atoms, we arrive at the number of atoms of each element contained in the molecule. This we express by a chemical formula.

Chemical formulas, then, are the final result of our process of stock-taking within molecules. When we write $\text{C}_2\text{H}_6\text{O}$ for the formula of alcohol, we mean that a molecule of alcohol, by the process of reasoning just described, has been found to contain two atoms of carbon, six atoms of hydrogen, and one atom of oxygen. Is this information sufficient to enable us to produce alcohol by combining atoms of carbon, hydrogen and oxygen in these proportions? Unfortunately for chemical industry it is not. For the atoms within a molecule are not thrown together into an unordered and indiscriminate heap. On the contrary, they are arranged in a definite way with respect to one another, which it is the task of chemistry to discover. Chemistry could not go very far toward duplicating nature's work in the laboratory, nor in producing new sub-

stances of even a simple sort, until something had been learned of the arrangement of atoms within a molecule with respect to one another. Mere stock-taking is not enough. Every molecule possesses an architectural plan, and some of these plans are very complicated. Even with a knowledge of the architectural plans of molecules the art of constructing them from individual atoms is rather difficult to master.

CHAPTER IV

THE BEGINNINGS OF ORGANIC CHEMISTRY

THE tid-bits that went into the witches' kettle in "Macbeth" were highly regarded, not only as stock for brewing charms, but as alchemical reagents. "Adder's fork and blind-worm's sting, lizard's leg and owlet's wing, scale of dragon, tooth of wolf," and all the rest—the more repulsive and outlandish a raw material the higher rose hopes of obtaining something rare and precious by subjecting it to destructive distillation in a retort.

Alchemical Efforts

This method of thought achieved one triumph, for the alchemist Brand, in 1674, by strongly heating a mixture of urine and white sand, produced phosphorus! Indeed, by heating all sorts of raw materials, including wood, bone, and fat, out of contact with air, the alchemists accomplished some chemical transformations which have since become the object of extended inquiry or have developed into important industries.

Yet all these alchemical attempts to take the citadel of the organic realm by direct assault led to nothing. Organic compounds are too subtly constructed to betray their composition to naive inquiry. No progress could be made until men turned from complex to simple objects. The key to the gateway of chemistry was to be found in a study of gases.

During alchemical times there were nevertheless occasional instances of synthesis by blunder. Some one stumbled on the fact that alcohol, when heated with sulfuric acid, produces ether. No one understood why

this should be. The real relationship between alcohol and ether remained hidden until 1850. As centuries passed occasional other organic substances were synthesized: sweet-smelling volatile liquids (ethyl nitrite, ethyl chloride, and ethyl acetate) by the action of nitric, hydrochloric, or acetic acids on alcohol; and impure acetone, by heating lead acetate, out of contact with air. Yet though these substances were repeatedly investigated during the later Middle Ages, no one ever got any inkling of how they were related to each other or how they happened to be brought into being by the processes that were used.

Some progress was made during alchemical times and the centuries that immediately followed in purifying organic substances. Nearly pure sugar was prepared by clarifying the juice of the sugar cane with lime and white of egg, then evaporating the solution until crystals of sugar separated. Alcohol was purified and concentrated by repeated distillation. One by one organic acids, found ready made in nature, were separated from admixture with other substances and made known. Acetic acid, which as vinegar had been known in a dilute and impure form since ancient times, was made to react with metallic oxides to form salts. From these concentrated acetic acid was prepared. It was the first organic acid to be made known in reasonably pure form. Succinic acid was prepared by distilling amber, benzoic acid by distilling gum benzoin, and formic acid by distilling ants.

Finally the Swedish chemist Scheele (1742-1786) showed how to prepare a large number of organic acids from plant juices, by first forming their lime or lead salts, then decomposing these with sulfuric acid. Thus he prepared citric acid from lemons, malic acid from sour apples, and oxalic acid from wood-sorrel. Other acids were prepared from sour milk,

The First
Organic
Syntheses

Scheele

and by the action of nitric acid on milk sugar. His experimental skill and keen powers of observation are evidenced not only by his ability to separate and distinguish between substances very much alike but by the fact that he discovered and carefully studied hydrocyanic acid gas—and lived!

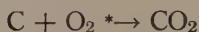
Scheele also discovered glycerine, which he prepared by decomposing vegetable oils by boiling them with lead oxide (litharge). He just missed the conclusion that the vegetable and animal fats and oils consist of glycerine in combination with organic acids. The honor of this discovery fell to the French chemist Chevreul, about half a century later.

In the inorganic field Scheele was famed as one of the three independent discoverers of oxygen (p. 8). He discovered nitrous oxide gas, now in familiar use in dental anesthesia. He discovered the element chlorine—a poisonous greenish-yellow gas which was to play a very important part in the development of organic chemistry some fifty or sixty years later. Chlorine makes up more than 60 per cent of ordinary table salt. The rest is sodium, a soft, light, silvery-white metal. Sodium will burn in chlorine gas, giving off torrents of white smoke. This presently settles as a white film on surrounding objects and proves to be common salt.

It was Lavoisier, in 1777, who first showed that alcohol, wax and many other products of the organic or living universe are composed of carbon, hydrogen, and oxygen. Berzelius suggested chemical symbols C, H, O, Cl and so forth, which are still used to represent the various elements; and introduced formulas, such as CHCl_3 and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, which have been employed since 1815 to show what sorts of atoms and how many of each are contained in a molecule of a given compound.

Chemists are also in the habit of using such formulas

to stand for the names of substances. Thus, instead of writing *carbon and oxygen combine to form carbon dioxide*, one may write simply:



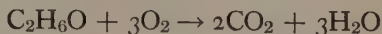
or



Such a statement is called an equation. The use of + and = signs in this way appears to be due to Lavoisier. Such a method of expressing chemical facts not only saves space but helps one to keep track of the different sorts of atoms that are concerned in the process. Moreover, each symbol stands for a definite weight of an element, and thus the equation as a whole indicates the relative weights of the reacting substances. The arrow or equality sign may be read "produce," "produces," "react with each other to produce," and so forth, as the case seems to require.

When ordinary (ethyl) alcohol, which may be written $\text{C}_2\text{H}_6\text{O}$, is burned, it combines with oxygen to form carbon dioxide and water. One molecule of alcohol will take three molecules (or six atoms) of oxygen from the air, and will produce two molecules of carbon dioxide and three of water. Therefore, in writing the equation we should indicate the *three* molecules of oxygen, the *two* of carbon dioxide, and the *three* of water, thus:

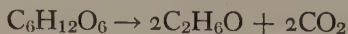
Balanced
Equations



Alcohol	Oxygen	Carbon dioxide	Water
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(1 mol.)	(3 mols.)	(2 mols.)	(3 mols.)
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Again, grape sugar, if fermented by yeast, is resolved into alcohol and carbon dioxide, and the equation is written thus:



Grape sugar	Alcohol	Carbon dioxide
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* We have already noted (p. 19) that ordinary gaseous oxygen is always written O_2 to indicate that a molecule of the gas contains two atoms.

Let the reader interpret this equation for himself, and see how every atom in the first formula is accounted for in the second two.

Equations which keep track of the number of molecules of each substance concerned in a chemical change are called *balanced equations*. Chemical textbooks tell how to perform the trick of balancing an equation which happens to be unbalanced. In principle that is very simple, too. You merely have to see that the atoms you start with are all accounted for among the molecules that you produce.

As early as 1825, illuminating gas was being manufactured by decomposing vegetable oils at high temperatures.

Faraday The product was compressed and sold in portable metal cylinders. When the gas had been drawn from these a small amount of liquid remained, which was submitted for examination to the English physicist and chemist Faraday. He found it to be a mixture of hydrocarbons (compounds containing only carbon and hydrogen); and one of its principal components was benzene, C_6H_6 , one of the most important substances in the whole realm of organic chemistry, and perhaps observed by Faraday for the first time. In 1845 a German chemist, A. W. Hofmann, noted the presence of benzene in coal tar. From that moment onward it occupied the attention of dozens of chemists and became the basis of a group of important industries.

Though Faraday is famed as the probable discoverer of benzene, this was almost his only contribution to organic chemistry. Shortly afterward he began researches in electricity and electrochemistry that were continued for more than twenty years. In the course of these he achieved so many important results that he will always be regarded as one of the great founders of modern electrical science and electrochemistry.

At the moment Faraday discovered benzene, a young German chemist, Justus von Liebig, was beginning work

that was to win him equal fame. We have already told something (p. 27) of Liebig's development of the method by which the percentage composition of organic compounds is determined, down to this very day. That, however, was one of his later achievements. His earliest efforts were with silver fulminate, a dangerously explosive compound that is formed by the action of alcohol on silver nitrate.

Liebig's experiments were conducted in his employer's apothecary shop. He had centered his interest on one of the most treacherous substances in the whole domain of chemistry. For silver fulminate sometimes permits one to deal familiarly with it, beguiling the careless worker into a sense of security. Again, it detonates violently at the slightest touch. The young chemist did not get very far in his researches before he produced an explosion that literally raised the roof.

Having escaped with his life, he turned for a time to safer pursuits, but the spell was too strong. Again and again he returned to silver fulminate, with an almost morbid interest. For a time he worked on the problem in Paris, as a pupil of Gay-Lussac, the successor of Lavoisier, and the leading French chemist of his day. In the end he won out. The percentage composition of this tricky compound was accurately determined, and its chemical properties thoroughly explored. At the age of twenty-one he had won wide recognition for his work, and was called as a professor to Giessen, where he remained for twenty-eight years, as the founder and director of the first chemical laboratory in the world for the instruction of students.

About this time another young German, Friedrich Wöhler, completed an analysis of a compound called silver cyanate, which gave this the very same percentage composition that Liebig had found for silver fulminate. Something surely was wrong! Letters were exchanged. In the end Liebig repeated

Wöhler's experiments, and got the same results as Wöhler.

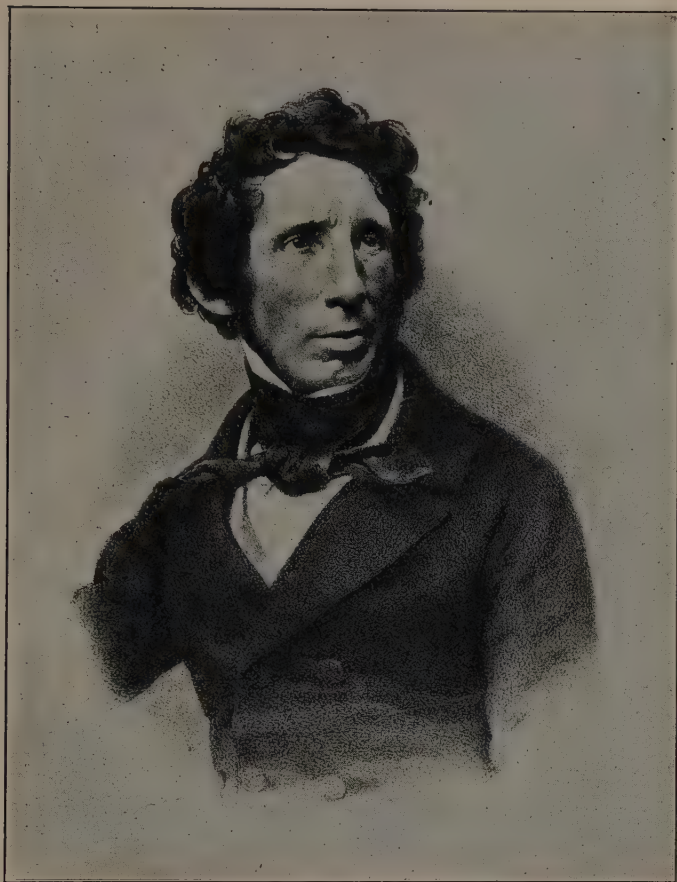
So, for the first time, it was demonstrated that two substances may possess the same chemical formula, that is, may possess molecules containing the same atoms, yet still be different. Neither Liebig nor any one else could immediately understand how this could be. In the end the conclusion grew that the differences between the two molecules were due to the fact that the atoms within them were differently arranged. It is the sort of difference that you produce in a room if you shift all the furniture into new positions.

The common interest that Liebig and Wöhler found in silver fulminate soon led them to become associated in some important joint researches, keeping in touch with each other by a frequent exchange of letters. Wöhler then turned to inorganic chemistry, leaving Liebig to devote himself to organic and later to agricultural chemistry. But the encouragement and inspiration which they found in each other never ceased while they lived. Their letters, since published, covered a period of more than forty years.

In 1828 Wöhler attempted to produce an inorganic salt, ammonium cyanate, by interaction of two other salts.

Wöhler Synthesizes Urea	To his very great astonishment, instead of the expected product he obtained urea, a white crystalline compound which is the chief nitrogenous excretory product of most mammals, and normally present in human urine, in a concentration of about 3 per cent.
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Though this discovery attracted no very great immediate attention, its significance was at length generally recognized. Here for the first time a substance previously known only as a product of the living or organic universe had been produced from materials that were commonly regarded as inorganic—in fact, from materials that were



Courtesy of Rudolf Lesch

FRIEDRICH WÖHLER

b. near Frankfort, 1800. His training in chemistry was entirely self-acquired, though he studied medicine under eminent teachers at Marburg and Heidelberg. Worked for a few months with Berzelius, at Stockholm. Discovered aluminum, beryllium and calcium carbide, synthesized urea, and developed the theory of radicals (jointly with Liebig). He was for forty-six years professor of chemistry at Göttingen, where he worked in full vigor until his death in 1882.

presently synthesized from the very elements carbon, hydrogen, nitrogen, and oxygen.

Within a few years Kolbe, one of Liebig's students, prepared acetic acid from materials that could be themselves produced directly from the elements. Other syntheses followed. It became very clear that plants and animals, in their manifold synthetic activities, make use of no mysterious special vital force that is peculiar to life. On the contrary, they employ only forces or sources of energy that are constantly used in the laboratory. Man may hope to produce any of Nature's products in the laboratory, if he does not count the cost in time or money that must be expended in learning how to do it.

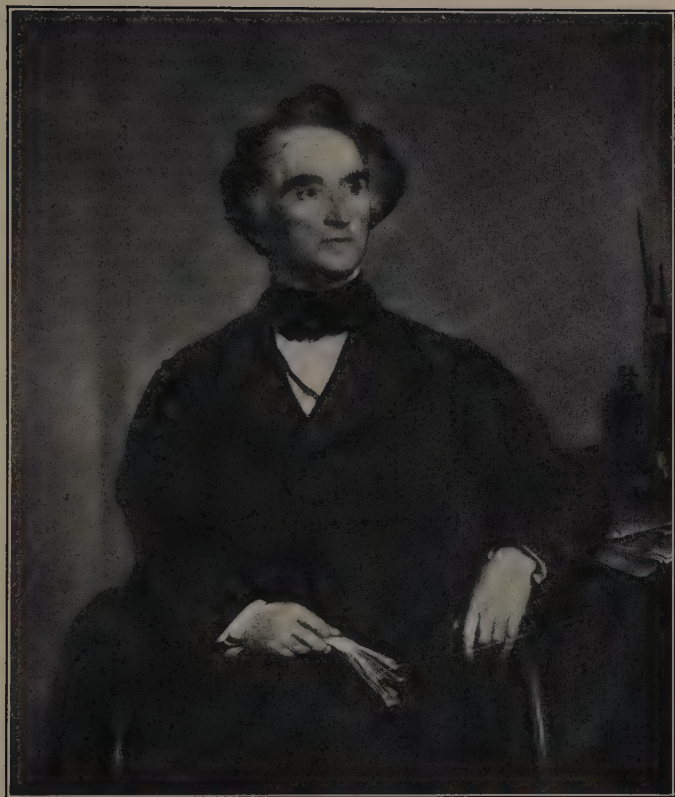
During the early years of the Nineteenth Century, while Berzelius and Liebig were perfecting the methods now in use for determining the composition of organic compounds, a beginning was made

Radicals

in discovering the relationships of these compounds to each other. In 1832 Liebig and Wöhler collaborated in an investigation that showed that the substances now known as benzaldehyde, benzamide, benzoic anhydride and benzoic acid can all be readily produced from each other, and have formulas that are very much alike. If we let R stand for the group of atoms C_7H_5O- , then

Benzaldehyde	= RH
Benzamide	= RNH_2
Benzoic anhydride	= R_2O
Benzoic acid	= $R_2O \cdot H_2O$

The same group of atoms R, namely C_7H_5O- , is found in all four substances. Here, for the first time, was a clear indication that when chemical changes take place in organic molecules, the molecules are not totally disrupted nor are the atoms rearranged into completely new groupings. On the contrary, certain groups of atoms stick together through thick and thin, in spite of violence done to the rest of the molecule. Such groups of atoms, forming parts of molecules, are called *radicals*.



Courtesy of Rudolf Lesch

JUSTUS VON LIEBIG

b. Darmstadt, 1803, the son of a dealer in dyes and chemicals. His early experiments with silver fulminate attracted the attention of the great naturalist, Humboldt, who found a place for him with Gay-Lussac, in Paris. Most of his work was done as professor of chemistry at Giessen. His activities in organic chemistry were followed by important contributions in agricultural chemistry and biochemistry. His later years were spent under the handicap of ill health in München, where he died in 1873.

Even before the work of Liebig and Wöhler several inorganic (non-carbon) radicals had been recognized, such as the ammonium radical, $\text{NH}_4\text{—}$, present in all ammonium salts, and the hydroxyl radical, —OH , present in all hydroxides:

NH_4Cl	NaOH
Ammonium chloride	Sodium hydroxide
$(\text{NH}_4)_3\text{PO}_4^*$	Ca(OH)_2^*
Ammonium phosphate	Calcium hydroxide

Before the work of Liebig and Wöhler, human resourcefulness was baffled by the infinite versatility of the element carbon. The chemical changes of the organic universe threatened to remain forever dark and mysterious. The discovery of radicals raised hope. Here in the midst of bewildering change, in the shuffling and re-shuffling of atoms into new arrangements, were groups of atoms that stood firm. If the radicals existent in organic compounds could only be recognized, it seemed likely that the relationships of these compounds to each other would be made plain, and that organic reactions might be carried forward with the easy assurance with which chemists had already learned to manipulate the inorganic acids, bases, and salts.

Small wonder, then that organic chemists during the years just following 1832 viewed the chemical reactions of organic compounds as a means for discovering what sorts of radicals are hidden within molecules. Liebig himself, in 1834, in reviewing work done by his great French rival, Dumas, at once recognized the existence, in ordinary alcohol and ordinary ether, of the ethyl radical, $\text{C}_2\text{H}_5\text{—}$. In the same year Dumas and Péligot discovered that the liquid obtained by heating wood in a closed retort contains a compound that has chemical properties

* Note the method by which we may indicate that two or more radicals of the same kind are contained in a given molecule.

very similar to those of ordinary (ethyl) alcohol. Thus the new compound was named *wood alcohol* or *methyl alcohol*,* and was recognized as containing the methyl radical, $\text{CH}_3\text{—}$. The discovery of other radicals followed in rapid succession, until dozens had been recognized.

Radicals brought order and system into organic chemistry, for it was soon recognized that organic compounds in general may be classified into groups or series of related compounds. The members of each series have similar chemical properties and differ from each other in possessing different radicals. Thus the *methyl radical*, $\text{CH}_3\text{—}$, the *ethyl radical*, $\text{C}_2\text{H}_5\text{—}$, or some similar radical, in combination with the *hydroxyl radical*, —OH , makes an alcohol. Altogether some hundreds of alcohols are now known. Again, a methyl, ethyl or any similar radical, in combination with the *carboxyl radical*, —COOH , makes an organic acid; and a pair of hydrocarbon radicals, in combination with an atom of oxygen, makes an ether.

Groups or
Series of
Compounds

<i>Radicals</i>	<i>Alcohols</i>	<i>Acids</i>	<i>Ethers</i>
$\text{CH}_3\text{—}$ Methyl	CH_3OH Methyl alcohol	CH_3COOH Acetic acid	$(\text{CH}_3)_2\text{O}$ Methyl ether
$\text{C}_2\text{H}_5\text{—}$ Ethyl	$\text{C}_2\text{H}_5\text{OH}$ Ethyl alcohol	$\text{C}_2\text{H}_5\text{COOH}$ Propionic acid	$(\text{C}_2\text{H}_5)_2\text{O}$ Ethyl ether
$\text{C}_3\text{H}_7\text{—}$ Propyl	$\text{C}_3\text{H}_7\text{OH}$ Propyl alcohol	$\text{C}_3\text{H}_7\text{COOH}$ Butyric acid	$(\text{C}_3\text{H}_7)_2\text{O}$ Propyl ether

By classifying organic compounds into such series of compounds the study of organic chemistry is very much simplified, for within each series we need make a particular study of only one or two compounds that serve as types for all the rest. When we know what methyl and ethyl alcohol will do in the presence of specified chemical reagents, we may very largely anticipate the

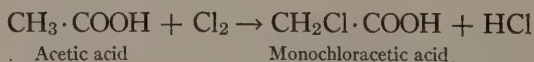
* Since renamed *methanol*.

behavior of propyl alcohol and of alcohols in general. The two hundred thousand organic chemical compounds that have been discovered are really less impossible to know intimately than two hundred thousand individual human beings, for they fall more sharply into classes or groups, and in each group a chosen representative may speak for all the rest.

Two years after the discovery of the first organic radical, chance disclosed new facts which were presently to reveal a new point of view. It was the year 1834. Under the light of wax candles guests were gathering for an evening at the Tuileries. All the elegance was assembled which fashion had just created: tall silk hats, close-fitting white pantaloons, tight stays and sweeping skirts. Then it was discovered that the air was filling with the choking fumes of hydrochloric acid—perhaps doubly discomforting to ladies in tight stays. We may imagine that the party broke up early.

Dumas, who was asked to investigate the matter, found that the wax from which the candles were made had been bleached with chlorine; and presently confirmed an earlier observation of Gay-Lussac, that when wax is bleached by chlorine a portion of its hydrogen is replaced by chlorine. The product is a chlorinated wax, which gives off hydrochloric acid fumes when it is burned.

This disclosure led to a study of the action of chlorine on other organic compounds; and it was presently found that chlorine may often be exchanged for hydrogen, atom for atom, and step by step. Thus when acetic acid is treated with a limited quantity of chlorine, the product is monochloroacetic acid:



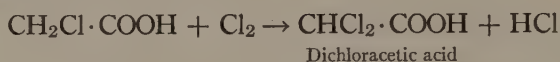
Note what has happened: An atom of hydrogen has been removed from acetic acid and an atom of chlorine



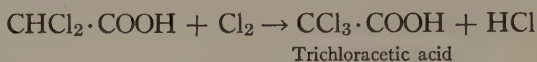
THE WORLD OF FASHION MEETS CHLORINATED WAX, 1834

has been put in its place. Incidentally, the hydrogen thus removed combines with chlorine to make hydrochloric acid gas, HCl.

If the monochloroacetic acid thus prepared is treated with a further quantity of chlorine, one more atom of hydrogen is removed from the molecule and an atom of chlorine put in its place:



Then with more chlorine we may do the same thing again:



Here the process stops. No further treatment with chlorine will displace the atom of hydrogen that still remains in trichloroacetic acid.

Such a replacement of hydrogen by another element, atom for atom, is called *substitution*. It was soon found that the substitution of chlorine or bromine for hydrogen often leaves the general chemical properties of the compound unchanged. The three chlorinated acetic acids are still acids, and indeed more active ones than acetic acid itself; and chloroform, CHCl_3 , derived by substitution of three chlorine atoms for three hydrogen atoms in methane, CH_4 , resembles methane in being neutral and conspicuously inactive chemically. Thus Laurent, a pupil of Dumas, advanced an idea which Dumas himself presently championed: When chlorine or bromine is substituted for hydrogen, it enters the organic molecule in such a way as to take the place and play the part of the hydrogen which is displaced. It is as if one or more beams of a building were to be replaced by suitable beams of a different material. The building would still stand firm.

Substitution revolutionized organic chemistry. For the radicals of Liebig and his school were no longer unalter-

able entities, but groups of atoms that might in part and on occasion be replaced by atoms of a different kind. Here, moreover, was the spectacle of hydrogen, an electropositive element, being replaced by the electronegative chlorine. Berzelius, who first classified elements as electropositive and electronegative, according to the sign of the electric charge that their atoms sometimes carry, refused to grant this possibility, and remained to the end of his days an enemy of the theory of substitution.

The years just following the discovery of substitution were years of conflict, in which the views of Liebig and

Laurent and
Gerhardt

Berzelius gradually gave way under the impact of newer ideas, advanced by Dumas, his pupil Laurent, and Liebig's pupil Gerhardt. The struggle was personal and bitter. Yet the contestants did not relax their efforts in the laboratory while they engaged in debate. On the contrary, they pursued their researches with more than common vigor, each in the hope of discovering pertinent new facts to confound his adversaries. Meanwhile, other workers added new compounds and groups of compounds to the list of those already known. Organic chemistry seemed about to be overwhelmed by its own productive efforts, for lack of any simplifying general point of view.

From the confusion of these years (1834-1842) there came a few definite advances. Laurent helped to make clear the distinction between atoms and molecules that is recognized today. Then Gerhardt, by some shrewd observations, arrived at chemical formulas as they are now written. All the progress which we have recorded was made in spite of the handicap that organic formulas, as they were first written, were nearly all in error, owing to the use of a false system of atomic weights. Unfortunately, few adopted Gerhardt's new system of formulas. Sixteen years more were to pass before the chemical world, through the efforts of Cannizzaro, perceived how molecular weights and true formulas might be definitely

established through an application of Avogadro's principle (p. 17).

Having established true formulas, Gerhardt next, at the age of twenty-six (1842), was able to classify organic compounds into series of compounds as they are recognized today. Plainly, organic chemistry as a science was getting under way.

The earliest syntheses of organic substances—that is, their earliest production from simpler substances—were the result of chance observations during the Middle Ages. Scheele, toward the end of the Eighteenth Century, made noteworthy additions to the list of organic substances then known. Then chemical equations were introduced to represent chemical changes.

Soon after 1828 it became clear that two substances might have the same chemical formula yet possess different properties, presumably because the atoms that composed the molecule were differently arranged with respect to each other in the two cases. The most important problem before the organic chemists of that time was, therefore, to determine the manner of arrangement of the atoms within each kind of molecule. A beginning was made when it was observed, in 1832, that certain groups of atoms remained together in spite of changes in other parts of the molecule. Yet it was almost immediately noted (1834) that hydrogen atoms—even those within a radical—might often be replaced by atoms of chlorine or bromine. Progress during these years was hindered by the fact that the formulas of most organic compounds were incorrectly written, due to failure to apply correct principles in establishing molecular weights.

CHAPTER V

A HIDDEN KEY

IT WAS now mid-century. Twenty-one years had passed since the discovery of organic radicals, and nineteen years since the discovery of the principle of substitution. Organic compounds, though still relatively few in number, were definitely arranged in series of related compounds, as we study them today. It was recognized that the atoms within molecules are connected with each other or placed with respect to each other in definite arrangements, and that differences in the arrangement of their atoms made it possible for two substances to possess the same chemical formula and yet be different from each other.

Just what the arrangement might be in any particular case, no one could say. At most, it appeared that here and there a certain group of atoms—a radical—tended to remain together in as close an association as any three musketeers. Yet faith in this tenet was somewhat shaken by the discovery that atoms of chlorine or bromine might on occasion step right into a radical and play the part of atoms of hydrogen. One might only expect the clannishness of the atoms within a radical to keep them together if they were not too sorely tempted to take part in an exchange.

The efforts of many workers, meanwhile, were creating new compounds by the thousand that ever seemed to become more complex. The worst of it all was that chemists were now losing contact with each other; for since the principle by which we now establish molecular weights (p. 18) had not

Mid-Century

Babel

yet been recognized, different chemists used different formulas for one and the same substance. The time was fast approaching when the members of the school of Gerhardt and Laurent would no longer be understood by those who still adhered to the system of Berzelius. It was chemical Babel. The work of the builders seemed about to be halted, for lack of a common tongue.

Yet Gerhardt, ever clear-thinking, shrewd, and self-consistent, had come into possession of true formulas, as we know them today, in spite of all handicaps. His next contribution was to show that many complex organic compounds appear quite simple, if we view them in comparison with four simple inorganic substances: hydrogen, hydrochloric acid, water, and ammonia. It is as if he had said: "Higher mathematics appears less complex if we show how it has developed from the four simple operations of arithmetic."

Let us begin with hydrogen, H_2 . Gerhardt wrote it $\begin{smallmatrix} H \\ H \end{smallmatrix} \}$. If we think of one of the two atoms in the hydrogen molecule as being replaced by an ethyl radical, C_2H_5- , we get $\begin{smallmatrix} C_2H_5 \\ H \end{smallmatrix} \}$, which is a well-known gas, ethane. If we replace both the hydrogen atoms in $\begin{smallmatrix} H \\ H \end{smallmatrix} \}$ by ethyl radicals we get $\begin{smallmatrix} C_2H_5 \\ C_2H_5 \end{smallmatrix} \}$, which is another well-known gas, butane.

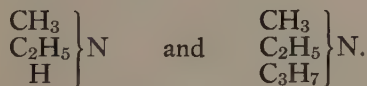
Next let us consider hydrochloric acid gas, HCl , which Gerhardt wrote $\begin{smallmatrix} H \\ Cl \end{smallmatrix} \}$. If we think of the hydrogen atom as being replaced by the ethyl radical, we get $\begin{smallmatrix} C_2H_5 \\ Cl \end{smallmatrix} \}$, which is ethyl chloride, known since the Middle Ages.

Again, from water, H_2O , which Gerhardt wrote $\begin{smallmatrix} H \\ H \end{smallmatrix} \} O$, we may derive $\begin{smallmatrix} C_2H_5 \\ H \end{smallmatrix} \} O$. This is ordinary (ethyl) alcohol,

which we have previously written $\text{C}_2\text{H}_6\text{O}$. Or, if we think of both the hydrogen atoms of water as being replaced by ethyl groups we have $\left. \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\} \text{O}$, which is ethyl oxide, or ordinary (ethyl) ether.

Finally, from ammonia, NH_3 , which Gerhardt wrote $\left. \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{N}$, we may derive three different compounds called amines, $\left. \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{H} \end{smallmatrix} \right\} \text{N}$, $\left. \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\} \text{N}$, and $\left. \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\} \text{N}$, according as we consider one, two, or three hydrogen atoms of ammonia as being replaced by ethyl groups.

We might similarly view methyl compounds as being derived by the replacement of hydrogen atoms of H_2 , HCl , H_2O , and NH_3 by methyl groups, CH_3 —; and so on for other compounds and radicals. Moreover, if one of the hydrogen atoms in water were replaced by a methyl radical, CH_3 —, and the other by an ethyl radical C_2H_5 —, we would have methyl ethyl ether $\left. \begin{smallmatrix} \text{CH}_3 \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\} \text{O}$, a “mixed ether.” With two or three different radicals replacing hydrogen atoms in ammonia, $\left. \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{N}$, we would have “mixed amines,” such as



Briefly, then, Gerhardt referred organic compounds to *four simple inorganic types*, in which hydrogen atoms might be replaced by organic radicals. His earlier efforts had grouped organic compounds into groups or series of chemically similar compounds. Now, he showed how these series were related to each other. For example, the

relationship of alcohol $\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{H} \end{array} \bigg\} \text{O}$ to ether $\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \bigg\} \text{O}$ became clear.

We should emphasize that it is not actually possible to replace hydrogen atoms by radicals, except by very roundabout processes. Gerhardt's achievement was in comparing, not in preparing. It was armchair chemistry. Yet his formulas did have the immediate practical result of suggesting new methods for producing well-known compounds from each other, thanks to the clearer view that he presented of their interrelationships. Moreover, his formulas suggested some compounds, such as the mixed ethers and simple and mixed amines, which had never yet been prepared, and so led to their discovery. Gerhardt was a great experimentalist, but his most famous contributions were the result of quiet reflection. The armchair had rendered distinguished service in aid of the laboratory, and chemical science pressed forward with ever-quickenning pace.

And now the successors of Boyle, Priestley, Scheele, and Lavoisier in their own turn passed from the stage.

A New
Setting for
New Events

Berzelius died in 1848. In the same year Dumas was diverted from his chemical studies by the political revolution in France, and devoted himself for twenty years thereafter to public service, becoming a member of the National Assembly, senator, director of the mint, and president of the municipal council which was entrusted with the task of making Paris a modern city.

Liebig, too, had long since withdrawn from active work in organic chemistry, and was making important discoveries in agricultural and physiological chemistry, to be related hereafter. The two clairvoyant geniuses, Laurent and Gerhardt, died prematurely, aged 46 and 40, many years before their great masters. There was need for a new group of workers.

Two new leaders now appeared: the English chemist

Frankland and the German chemist Kekulé, both pupils of Liebig. Frankland early won fame as the discoverer of some extraordinary organic compounds containing zinc, which are extremely poisonous, volatile liquids, that catch fire when they are exposed to the air. One would think this a most unpromising behavior, yet these substances were soon found to be very useful reagents for the preparation of other organic compounds of practical importance, such as the dyestuffs. Later, similar bismuth, thallium and magnesium compounds were prepared. The magnesium compounds especially have proved indispensable in carrying out the intermediate steps of some of the most startling recent achievements of practical chemistry (p. 115). All this grew out of Frankland's attempt to discover what happens when organic chlorides are treated with zinc dust.

In 1852 Frankland noted that an atom of nitrogen, phosphorus, or arsenic nearly always combines with *three* or with *five* other atoms—with three in NH_3 , PCl_3 , AsCl_3 , AsH_3 ; and with five in NH_4I , NH_4Cl , PCl_5 , PH_4I . In other words, each atom of nitrogen, phosphorus or arsenic possesses a combining capacity, later called a *valence*, of three or five.

Other chemists made similar observations. In water, H_2O , we see that oxygen has a combining capacity or valence of two, since one atom of oxygen combines with two hydrogen atoms; and aluminum in aluminum chloride, AlCl_3 , has a valence of three, since one atom of aluminum combines with three atoms of chlorine.

Presently Couper, in England, and Kekulé, in Germany, applied the idea of valence to organic radicals. Kekulé first observed that the organic radicals methyl, CH_3 —, and ethyl, C_2H_5 —, each have a valence of one, since they combine with one other atom to form such compounds as CH_3Cl and $\text{C}_2\text{H}_5\text{I}$. Certain other radicals, however, were observed to have valences of two or three,

Organo-
Metallic
Compounds

Valence

such as the glyceryl radical $\text{C}_3\text{H}_5\equiv$,* which can combine with three chlorine atoms or three hydroxyl groups, to form such compounds as $\text{C}_3\text{H}_5\text{Cl}_3$ or $\text{C}_3\text{H}_5(\text{OH})_3$.†

Events were now moving toward a most important disclosure, which was to furnish the key to the details of the inner structure of organic molecules. It was the year 1858, noteworthy for Cannizzaro's exposition of the manner in which molecular weights might be established.

Kekulé
Finds the
Hidden Key

Kekulé was reviewing compounds of carbon, classified by types. He noticed that to the four simple inorganic types of Gerhardt should be added a fifth, that of methane or marsh gas, CH_4 . If we think of its four hydrogen atoms as being replaced by chlorine atoms, hydroxyl groups, or methyl radicals, we have a series of familiar compounds.

Ordinary formulas:	CH_4	CHCl_3	CH_3OH	$\text{C}_2\text{H}_5\text{OH}$
Otherwise written:	$\text{C} \begin{Bmatrix} \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{Bmatrix}$	$\text{C} \begin{Bmatrix} \text{H} \\ \text{Cl} \\ \text{Cl} \\ \text{Cl} \end{Bmatrix}$	$\text{C} \begin{Bmatrix} \text{H} \\ \text{H} \\ \text{H} \\ \text{OH} \end{Bmatrix}$	$\text{C} \begin{Bmatrix} \text{CH}_3 \\ \text{H} \\ \text{H} \\ \text{OH} \end{Bmatrix}$
	Methane	Chloroform	Methyl Alcohol	Ethyl Alcohol

These formulas at once suggested to Kekulé that carbon itself must have a valence of four, since it can combine with four other elements or radicals, each with a valence of one. Thus it suddenly became clear to him that each carbon atom should display a valence of four, even when it combines with other carbon atoms, in forming complex radicals, or molecules. Carbon, in a word, is *tetravalent*. This simple idea was the long-sought hidden key.

*The valence of an element or radical is often represented by horizontal or vertical strokes placed after its symbol or formula. Thus $\text{C}_3\text{H}_5\equiv$ and Fe''' indicate a valence of three.

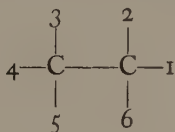
† This is glycerine, recently renamed glycerol, which was discovered by Scheele.

Kekulé and Frankland were eye-minded. They belonged to the class of persons who think best with pencil in hand, making sketches. To indicate that carbon has a valence of four, Frankland pictured carbon atoms as each possessing four hooks, or strokes, called *valence bonds*, to link them up with other atoms. Then if two such atoms, each with four valence bonds,

Valence
Bonds

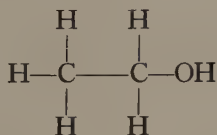


draw close together and connect with each other, two valence bonds will be used in linking them together:



Let us think of each of the two carbon atoms as being possessed of four hands, reaching out to connect with other atoms. Two linking hands clasp each other. There then remain six unattached hands or valence bonds, here numbered.

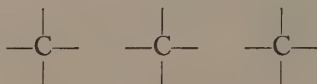
We can attach any other atoms that we please to the six remaining valence bonds. Attach five hydrogen atoms and a hydroxyl radical, $-\text{OH}$, and we have the formula for ordinary (ethyl) alcohol:



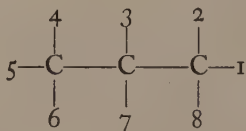
Still we must emphasize that this again is only armchair chemistry. We have not revealed any practical method for producing alcohol illicitly.

So, from Kekulé's perception that carbon has a valence of four, and from Frankland's use of valence bonds to represent that fact, there came chemical formulas of a new kind, called *graphic formulas*, which showed the order in which atoms are linked together within molecules. As a further illustration, let us take three carbon atoms, each with its four valence bonds:

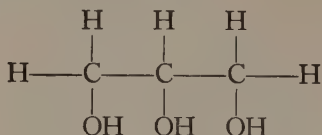
Chemical
Formulas
of a New
Kind



If we link these together we must use four valence bonds in the process, and eight valence bonds, here numbered, will be left over:

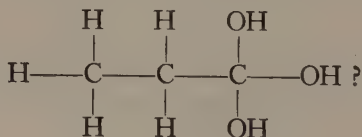


If we use five of these valence bonds to attach hydrogen atoms and three to attach hydroxyl groups, we have the formula of glycerine (glycerol):



But hold! How do we know that the three hydroxyl groups which glycerol contains are really attached to three different carbon atoms? May they not all three be attached to a single carbon atom at the end of the chain:

Problem of
Position



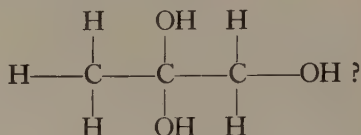


KEKULÉ DREAMS

"One fine summer evening I was returning by the last omnibus, 'outside,' as usual, through the deserted streets of the metropolis, which are at other times so full of life. I fell into a reverie, and lo, the atoms were gambolling before my eyes! Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion; but up to that time I had never been able to discern the nature of their motion. Now, however, I saw how, frequently, two smaller atoms united to form a pair; how a larger one embraced two smaller ones; how still larger ones kept whirling in a giddy dance. . . . The cry of the conductor: 'Clapham Road,' awakened me from my dreaming; but I spent a part of the night in putting on paper at least sketches of these dream forms."

—F. R. Japp, Kekulé Memorial Lecture, *Journal of the Chemical Society (London)* 1898, p. 100.

Or two of them to the middle carbon atom, and the third to a carbon atom at one end:

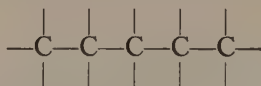


(There are still two other possibilities, which are left to the reader to suggest.)

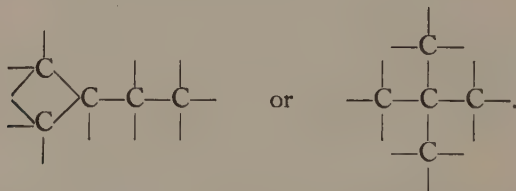
In the end, experience showed that it is only rarely that more than one hydroxyl group can be induced to enter into union with a given carbon atom. Of the several formulas that we have suggested for glycerol, the first was finally proved correct.

Thirty years had now passed since Liebig's comparison of silver fulminate with silver cyanate had shown that two substances may have the same chemical formula yet still be very different. Graphic formulas made it easy to see how such differences came about. It was plain that the chains of carbon atoms to which other atoms were attached may sometimes be simple, unbranched chains,

**Branched and
Unbranched
Chains**



and sometimes branched chains,



In either case, there are usually several different carbon atoms to which the substituting atom or group, such as

chlorine or hydroxyl, may be attached. Thus not merely two but many different substances may often be produced, of identical percentage composition, and identical molecular formulas, but with different graphic formulas, corresponding to different arrangements of atoms.

Compounds whose molecules are identical except that the atoms within them are differently arranged are called

Isomers *isomers*. The problem of determining how many isomers are possible for a given chemical formula is simply the problem of determining how many different arrangements of atoms are possible, in building a branched or unbranched chain of carbon atoms and attaching other atoms to it.

Kekulé's theory served as a guide in the preparation of thousands of new compounds which would otherwise long have remained undiscovered; for with an architectural plan in mind we can build straightforwardly. The essential truth of his theory is shown by the fact that in all the years that have passed since 1858, researches in organic chemistry have never brought to light more *chemically different* isomers of a given substance than the theory might have predicted in advance. Its worth is measured by its ability to stand the test of time; for the development of science is attended by a never-ceasing contest of ideas, in which only the fit survive.

The first clue to the arrangement of atoms within molecules came from the observation that the formulas of

Summary many organic compounds may be written as if derived from H_2 , HCl , NH_3 , and CH_4 , by replacing one or more hydrogen atoms by specified groups of atoms. It was then noticed that an atom of carbon may combine with four hydrogen atoms or four hydrocarbon radicals. Carbon, in brief, has a valence of four. This led to graphic formulas, in which each carbon atom is linked to neighboring atoms by four strokes or

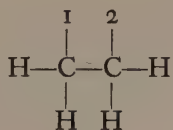
valence bonds. It then became evident that differences in the arrangement of atoms within the molecules may either be due to differences in the manner of linkage of carbon to carbon to form a carbon skeleton, or to differences in the positions on this skeleton at which other kinds of atoms are attached.

CHAPTER VI

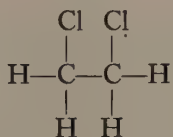
THE MYSTIC HEXAGON

DUMAS found that chlorine and bromine displace hydrogen from many organic compounds, and enter into the molecule in its stead. This was substitution (p. 48). Yet there are many compounds that absorb chlorine or bromine directly without losing any hydrogen. These came to be called *unsaturated compounds*—unsaturated because they are able to take up more.

When Kekulé brought out his theory, it was at once observed that unsaturated compounds have some unused valence bonds, which may be employed to attach atoms of chlorine or bromine. Thus ethylene, C_2H_4 , is represented as an unsaturated compound with two unused valence bonds (1, 2).

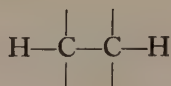


Ethylene should therefore combine directly with two chlorine atoms to form:

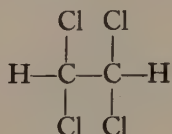


This is precisely what happens.

Acetylene, C_2H_2 , is represented as possessing four unused valence bonds:

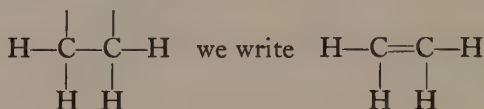


It should therefore combine directly with four chlorine atoms to form

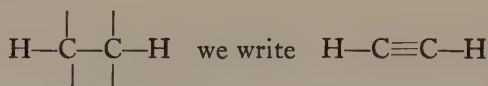


and it does. Kekulé's theory scored a triumph in predicting just how many chlorine atoms a molecule of a given unsaturated compound would prove capable of adding to itself.

At present it is customary to connect the unused valence bonds of unsaturated compounds with each other to form *double* or *triple* bonds. Instead of



and instead of



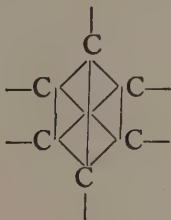
The double bond represents *two pairs* of joined bonds, and the triple bond, *three pairs*. But *one pair* is sufficient to hold two atoms together. Therefore every double bond includes a pair of valence bonds that are free to combine with something else; and the compound concerned may add two atoms of chlorine, bromine or hydrogen. Each triple bond represents two pairs of valence bonds that are free to combine with something else; and

the compound concerned may add four atoms of chlorine, bromine or hydrogen. In brief, a double or triple bond is the symbol of valence units waiting to be put to work.

Even in the time of Kekulé many compounds were known which contained hardly more than one atom of hydrogen for each atom of carbon. It seemed evident that they must have some unemployed valence units. Yet they failed to combine directly with chlorine, bromine or hydrogen except under special provocation (in the sunlight, or in presence of a catalyzer). Their unemployed valence units, if there were any, were not actively seeking employment. Double and triple bonds, which symbolized "valence units looking for work," clearly did not fit.

These hydrogen-poor, chemically inert substances, such as benzene, are now called *aromatic compounds*. They presented a problem which baffled Kekulé during nearly seven years. He must have considered it often, only to lay it aside. How could the aromatic compounds contain as little hydrogen as they did without being greedy for more? Yet the processes of thought do not cease when they sink below the threshold of consciousness. Kekulé's relation of the event makes plain that this problem also was finally solved by subconscious thought, which is haphazard and unorganized, yet persistent and unwearying, toiling in secret at the uncompleted tasks of genius.

The winning thought (1865) was that the six carbon atoms of benzene, C_6H_6 (the simplest aromatic compound) formed a ring or hexagon. Later workers added other details:



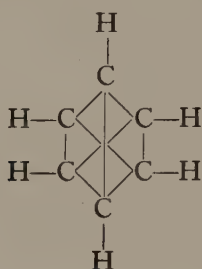
"I was sitting, writing at my text-book; but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of the kind, could now distinguish larger structures, of manifold conformation: long rows, sometimes more closely fitted together; all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis."

—F. R. Japp, Kekulé Memorial Lecture, *Journal of the Chemical Society (London)* 1898, p. 100.



THE BENZENE RING

In forming this ring we shall need to use two of the four valence bonds of each carbon atom to link it with its two neighbors. A third bond connects with a hydrogen atom, and a fourth connects across the center of the ring with a carbon atom on the opposite side. Thus all six carbon atoms are linked together in intimate union.



This is the famous benzene ring, which helps us to understand why benzene, in spite of its small content of hydrogen, has no apparent desire to combine with any more. Benzene does not behave as an unsaturated compound because it has no unemployed valence bonds. They are all in active service in binding the six carbon atoms together into a compact group.

Kekulé then showed that many other familiar aromatic substances were derivable from benzene—at least on paper—by replacement of some of the hydrogen atoms of benzene by other atoms or groups. Thus in a single effort he cleared up most of the mystery that had surrounded this important class of compounds. His work was immediately of the greatest practical significance in suggesting methods for preparing aromatic substances from each other, now that their interrelationships had been made plain. Today the great synthetic dyestuff industry and our knowledge of the chemical structure of numerous compounds of medicinal importance rest

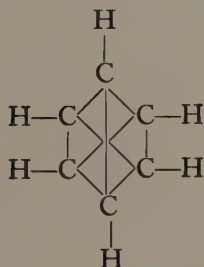
**Aromatic vs
Aliphatic
Substances**

upon this achievement of the subconscious mind of Kekulé.

At the present moment, aromatic compounds containing benzene rings or related rings make up more than half of the organic substances—estimated to be over 300,000 in number—that have been discovered. The open-chain compounds, such as alcohol, acetic acid and glycerol, are termed *aliphatic* (Greek: fatty) compounds, since the animal and vegetable fats and oils belong in this group.

The Benzene
Ring
Simplified

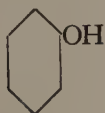
In modern chemical textbooks the benzene ring usually appears in a simplified form. The six centrally directed valence bonds and even the carbon and hydrogen atoms are left to the imagination. Instead of



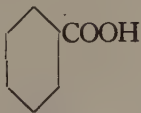
we print simply



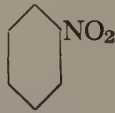
Then if we attach groups or atoms to any of the six corners of the ring, we mean that the hydrogen atoms which normally stand at these corners have been *replaced* by these groups or atoms. Examples:



Phenol
(Carbolic acid)



Benzoic
acid



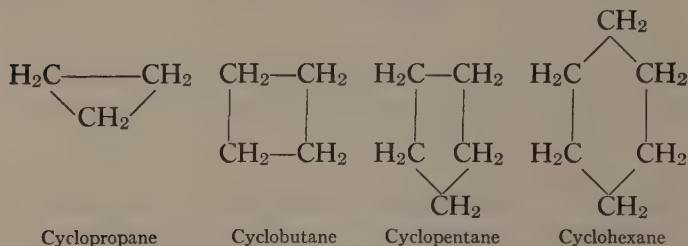
Nitrobenzene

In these a hydrogen atom in benzene has been replaced by $-OH$, $-COOH$, and $-NO_2$, respectively.

The discovery of the structure of benzene led to the

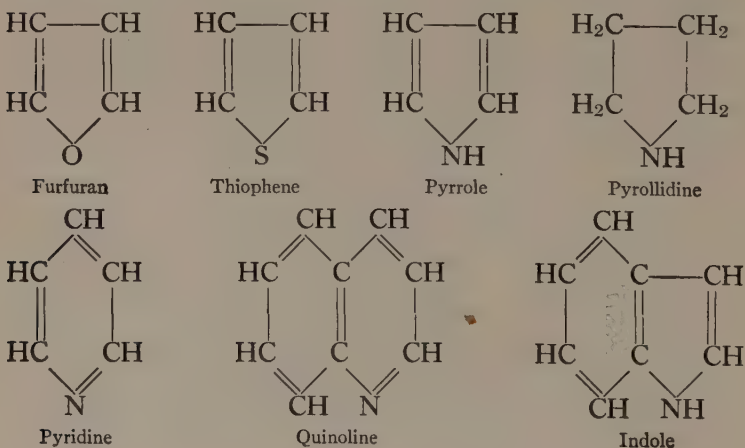
search for other sorts of rings of atoms. At present we know hydrocarbons consisting of rings or cycles of three to six carbon atoms, with all sorts of substituted derivatives:

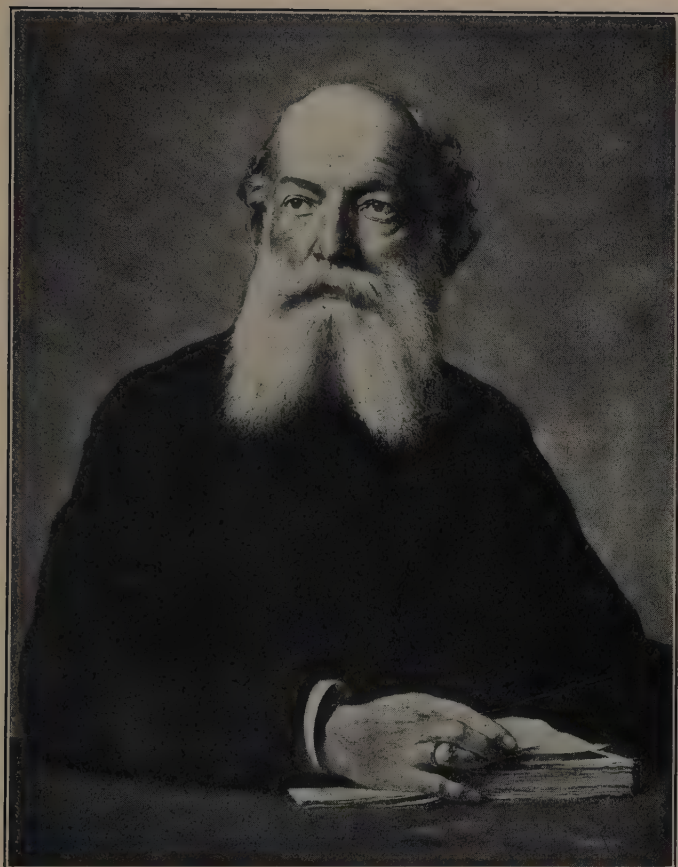
Some Other
Rings



Such compounds have few properties in common with benzene, for their rings are multiples of the group >CH_2 rather than >CH . Their nearest relatives are in fact the open-chain, saturated hydrocarbons from which they are named. Cyclohexane is interesting as being derivable from benzene by direct addition of six atoms of hydrogen, through the action of vigorous reducing agents.

The greatest interest, however, attaches to rings containing not only carbon but other elements, such as oxygen, sulfur or nitrogen:





Courtesy of Rudolf Lesch

AUGUST KEKULÉ

b. Darmstadt, 1829; pupil of Liebig at Giessen. Attended lectures by Dumas in Paris, and became an intimate friend of Gerhardt. Worked for a time in Switzerland, then in London, where he developed his idea of the tetravalency of carbon. Afterward served as *Privatdozent* at Heidelberg, then as professor of chemistry at Ghent, where he wrote his famous paper on the benzene ring. In 1867 he became professor of chemistry at Bonn, where his later years were spent in declining health.

d. Bonn, 1896.

As our knowledge of these compounds and their derivatives has increased, their importance has come to rival that of benzene itself. Some of them have entered into the manufacture of dyestuffs. Others are constituents of the proteins of our food, and play an important part in the processes of digestion, assimilation and excretion. Moreover, pyridine and quinoline, pictured above, are built into the molecular structure of many alkaloids (p. 298)—an awe-inspiring group of compounds which includes powerful poisons like strychnine and brucine, together with the procaine and novocaine of the dentist's chair, morphine, nicotine, and the substances responsible for the mild stimulation that many of us find in coffee, tea or cocoa.

It would be interesting to relate the story of investigators who devoted many patient years to determining the structure of these groups of substances and to their syntheses from simpler ones. More than one worker was content to spend most of his active life in studying some one group of compounds. Yet here, as elsewhere in this book, we can hardly do justice to the work of the host of laborers of less than the highest fame, without overburdening our narrative with historical details. The development of chemistry was less the result of the efforts of a few men of unrivaled genius than our treatment has made it appear to be. During the generation when Gladstone, Bismarck, Cavour and Napoleon III occupied the center of the European political stage, a company of quiet men, almost unknown to fame, were slowly amassing the detailed information that was to serve as the basis for the scientific and industrial development of our modern world.

From the first analyses of organic compounds at the hands of Lavoisier to the work of Kekulé on the benzene ring, some eighty years passed by. Let us review the steps by which organic structural formulas, the architectural plans of molecules, were revealed during these eighty years.

- 1777 Lavoisier showed that most organic compounds consist of carbon and hydrogen or carbon, hydrogen, and oxygen.
- 1815 Berzelius derived the first organic formulas from the results of *analysis by combustion*.
- 1828 Wöhler synthesized urea. This was the first production of an organic substance by artificial means from purely inorganic material. This and other syntheses proved that organic substances do not owe their origin to any special "vital force," but may be synthesized by the same general methods that apply to inorganic compounds.
- 1831 Liebig perfected the method of analysis by combustion.
- 1832 Liebig and Wöhler published their paper on the radical of benzoic acid. Organic compounds, from this time onward, were considered as containing groups of atoms which might remain unchanged, in spite of alterations in the remainder of the molecule.
- 1834 Dumas discovered that the hydrogen of organic compounds may often be replaced by chlorine or bromine, without seriously altering their general properties. Thus organic molecules were recognized as having a definite mechanical structure, like the framework of a building, in which one kind of atom might sometimes be replaced by another.
- 1842 Gerhardt classified organic compounds into homologous series.
- 1842-1853 Rapid experimental progress was made and new methods of synthesis discovered that disclosed many new compounds and groups of compounds.
- 1852 Gerhardt correlated the new compounds by referring them to four inorganic type-compounds. The new syntheses were then easily explained as

accomplished by exchanges of atoms or groups of atoms, of the sort long familiar in inorganic chemistry. As a result of such reactions, hydrogen might be replaced, step by step, by radicals. This was substitution in a broader sense than that studied by Dumas.

- 1857 Kekulé recognized the fact that different organic radicals differ in valence.
- 1858 Cannizzaro showed how true formulas may be derived, based on molecular weights in harmony with a principle announced by Avogadro nearly fifty years before. A few workers, particularly Laurent and Gerhardt, had arrived at true formulas before this; others continued to use inaccurate ones for some years thereafter.
- 1858 Kekulé recognized carbon as being tetravalent; and conceived of carbon compounds as being formed by the addition of other kinds of atoms to chains or skeletons of carbon atoms.
- 1865 Kekulé introduced a ring or hexagon of six carbon atoms to explain the properties of benzene, and explained aromatic compounds as being derived from benzene.

In retrospect, we can see that each development led naturally to the next. Simple formulas gave place to those in which certain groups of atoms (radicals) were set apart from the rest. Then substitution was discovered; chlorine or bromine for hydrogen, and radicals for hydrogen. Different radicals were next recognized as having different valences, and the carbon atom itself as having a valence of four. Thus the internal structure of the radicals themselves, and finally that of molecules as a whole became clear; first for aliphatic and then for aromatic compounds. Through eighty years of effort the architecture of molecules was revealed; and the way stood open to secure and rapid progress.

CHAPTER VII

PLANS AND SPECIFICATIONS

Now that the reader knows what organic formulas mean and how they were developed, he may readily follow wherever our story leads. With the introduction afforded by the six preceding chapters, he should be able to catch the drift of things in any elementary organic textbook. In what comes after this he may select what suits his interest.

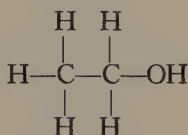
Retrospect
and
Anticipation

The present chapter is intended for the reader of more than average earnestness, who may wish to know something of the manner in which the structural formulas of a few common substances were worked out. We are anxious not to give the impression that the complicated structure of such a molecule as camphor was derived by any lucky guess, dream or sudden inspiration. Its plans and specifications had to be discovered by long years of experimentation.

By devoting a few pages to such details, we should leave the reader with a more vivid sense of the reality of molecules and molecular plans of architecture, as we have represented them. We arrive at a structural formula for camphor, by years of systematic research, and then use this plan as a working guide for further effort, which at length actually produces camphor from turpentine. Thus we know that the molecular plan which directed our work was based on reality.

Let us begin with simpler compounds, however. First, consider ethyl alcohol. Its percentage composition and molecular weight correspond to the formula C_2H_6O (p. 30). If we treat it with phosphorus trichloride, PCl_3 , a hydrogen atom and an oxygen atom of the alcohol are *removed together*, and replaced by chlorine. Thus we obtain ethyl chloride, C_2H_5Cl . This result suggests that one hydrogen atom and one oxygen atom in the original alcohol are in such intimate union with each other that if the oxygen atom is displaced from the molecule the hydrogen atom has to go with it. In other words, the alcohol molecule contains a hydroxyl group, $-OH$. Instead of C_2H_6O we may therefore write C_2H_5OH .

If we now give each carbon atom four valence bonds to connect with hydrogen or hydroxyl, we have the graphic formula of alcohol (p. 57):



In practice we find that all the most essential information in this graphic formula is retained if we condense it somewhat, to save space, and write



Such condensed graphic formulas are called *structural formulas*.

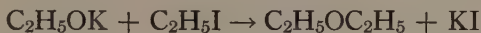
Two questions commonly asked by the chemical novice:

Are these formulas for alcohol all equally correct?

Yes, so far as they go. Yet C_2H_6O fails to show that alcohol contains a hydroxyl group. Indeed, this formula may leave us in doubt which substance is meant. For methyl ether is likewise C_2H_6O , but with its atoms differently arranged, as given by the structural formula CH_3OCH_3 .

When is the graphic or structural formula for alcohol preferred to the simple formula C_2H_5OH ? Whenever we need to show which particular hydrogen atoms are being replaced by atoms of other kinds, when alcohol is chemically altered.

Let us next see how the formula of ether has been derived. When metallic potassium is added to alcohol it displaces hydrogen, forming a white solid, potassium ethylate, C_2H_5OK . It can readily be shown that the hydrogen atom which has here been replaced by a potassium atom is that present in the hydroxyl group of the alcohol. In 1850 the English chemist Williamson found that if potassium ethylate is heated with ethyl iodide, the product is ether and potassium iodide:

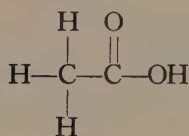


The reaction is most simply explained as an exchange of potassium (K) for ethyl (C_2H_5-). Thus ether must be $C_2H_5OC_2H_5$, which may also be written $(C_2H_5)_2O$, or $C_2H_5 \rangle O$, diethyl oxide. This is confirmed by the fact that ether does not react with phosphorus trichloride. It therefore contains no hydroxyl radical. In other words, its oxygen atom must be connected by two valence bonds directly with carbon.

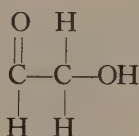
Acetic acid furnishes our next example. From the molecular weight and percentage composition of acetic acid we may derive the formula $C_2H_4O_2$ (p. 30). When we treat the acid with phosphorus trichloride, PCl_3 , we obtain a compound with the formula C_2H_3OCl . It is plain that here one oxygen atom and one hydrogen atom of the acetic acid have

taken their departure together and have been replaced by chlorine. We conclude that acetic acid, like alcohol, contains a hydroxyl group. Let us therefore write it $C_2H_3O(OH)$.

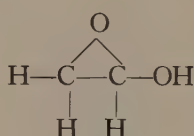
But carbon has a valence of four, oxygen a valence of two, and hydroxyl a valence of one. Let us hook the atoms together in such a way as to give each carbon atom four strokes or valence bonds to connect it with other atoms, oxygen two valence bonds, and the hydroxyl group one valence bond. If the reader will try this for himself he will soon discover that there are three possible ways of doing it. If the oxygen atom not in hydroxyl is attached by its two valence bonds to *the same* carbon atom as the hydroxyl group, the result is formula I, below. If it is attached to *the other* carbon atom, the result is II. If it is attached to *both* the carbon atoms at once, the result is III.



I



II

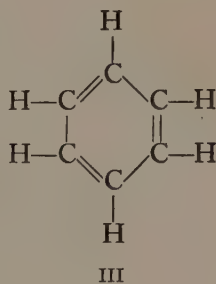
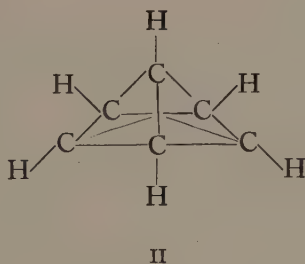
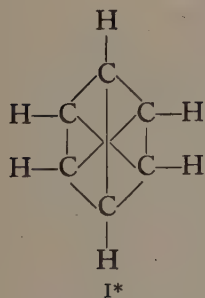


III

Which of these possible formulas for acetic acid is the true one? To settle that question, note that the three hydrogen atoms not in the hydroxyl group are all attached to *the same carbon atom*, in I; but in II and also in III, a part of them are attached to one carbon atom and a part of them to the other. Thus if a chlorine atom is substituted for a hydrogen atom, in formula I, to form monochloroacetic acid, the chlorine atom is foreordained always to become attached to the carbon atom *not linked to hydroxyl*. But in II and III, the chlorine may replace hydrogen that is attached to the one carbon atom or to the other, and the two products thus formed will be chemically different from each other.

Now all the efforts of synthetic chemists, from Dumas down to the present hour, have produced but *one* compound derived from acetic acid by the substitution of a chlorine for a hydrogen atom. Thus of the three different possible formulas for acetic acid, there is no doubt that I, more compactly written CH_3COOH , is correct. In brief, we note that chlorine, in replacing hydrogen in acetic acid, always replaces hydrogen that is attached to a given carbon atom; we conclude that there is no hydrogen on the other carbon atom. By analogy, if a passenger entering a subway train at a given station always becomes attached to a strap, we conclude that there are no seats.

Our final example is benzene. We have just seen that we may often determine which of several possible structural formulas for a given substance is the true one, by finding which of them accounts for the number of chlorine-substituted derivatives that can actually be prepared. It was this principle which ultimately led benzene to be considered as a simple, regular hexagon (I), rather than a triangular structure (II), or one possessed of single and double bonds in alternation (III).



* This formula was first suggested in 1887. It is usually written as a hexagon which has been compressed laterally; but this is merely to save space in printing.

For II should yield two different monochlorobenzenes, according as a hydrogen atom at a corner or at the mid-point of a side is replaced by chlorine. Yet in fact only one monochlorobenzene has ever been prepared. And III predicts the existence of more dichlorobenzenes than the intensive research in this field has ever been able to produce.

When other atoms or groups of atoms are substituted for hydrogen, around the benzene ring, we should like to know where they go. Do the substituting atoms go into adjacent positions (I), or are they spaced a third of the way around (II) or half way around (III)?

Spacing
Atoms Around
The Benzene
Ring



I

Adjacent
Ortho-dichloro-
benzene



II

Neighboring
Meta-dichloro-
benzene



III

Opposite
Para-dichloro-
benzene

It is easy to see that there may be three different isomers for all twice-substituted benzene derivatives, according as the substituting groups are adjacent, neighboring, or opposite. Whether the two substituting atoms or groups are alike or different, three different isomers are always known.

The problem, then, is to discover whether the two substituting atoms or groups in any given twice-substituted benzene derivatives are separated by a step, skip, or jump. Kekulé recognized this problem but failed to solve it. It demanded ten more years of incessant labor on the part of many investigators. Then the clue was furnished by Körner, a pupil of Kekulé. It was simply to

note how many thrice-substituted compounds can be prepared from a given twice-substituted compound.

Having disclosed the architectural plans of twice-substituted molecules, it was easy to pass from these to thrice-substituted molecules, and so on. With a few more years of effort, the spacing of the substituting atoms and groups round the benzene ring was worked out for a great multitude of aromatic compounds. By 1885—twenty years from the time of the first paper of Kekulé on the benzene ring—the problem of relative position was practically solved. Today you may buy many of these benzene derivatives in carload lots, with the substituting groups placed anywhere you specify. If you would have them in adjacent positions, ask for an *ortho* compound; in positions one step removed, a *meta* compound; in opposite positions, a *para* compound. Usually these prefixes are represented by their initial letters: *o*, *m*, *p* (as in *o*-cresol, *m*-cresol, *p*-cresol). The compounds thus distinguished, though of very similar chemical properties, are often physically quite different. One of them may be a solid, and the other two liquids of different boiling points. If you build them into dyestuffs or perfumes, the colors or odors that you get will generally be different, one from another.

If a compound happens to have a very complicated structure, we can often determine this only by reactions which tear down the molecule, step by step.

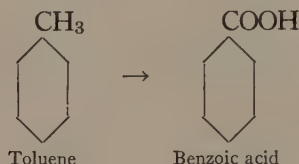
Two
Important
Principles

Then by examining the fragments we may perhaps guess what the original structure was like.

An important guide in the reasoning comes from the knowledge that *oxidation continues where it has once begun*. Thus if an alcohol group, -OH , is attached to a given carbon atom, oxidation will produce a ketone group, -CO ; or an aldehyde group, -CHO ; or, finally, a

carboxyl group, $-\text{COOH}$, in the very position that the carbon joined to the hydroxyl group occupied in the original compound.

Again, experience has taught that *oxidation strips away any chains of atoms that happen to be attached to a ring, leaving carboxyl groups, $-\text{COOH}$, in their stead.* Thus when the hydrocarbon toluene is oxidized, the result is benzoic acid:



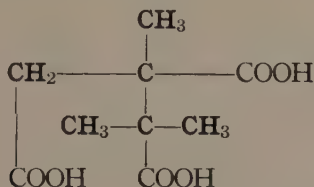
Note that the methyl group, $-\text{CH}_3$, has been converted into a carboxyl group.

Let us see how the two principles just given were applied in determining the structure of camphor. Dumas found that the percentage composition of camphor corresponds to the formula $\text{C}_{10}\text{H}_{16}\text{O}$. When it is heated with phosphorus pentoxide, the main product is a hydrocarbon (*p*-cymene), which oxidation converts into terephthalic acid, which is known to have the formula:



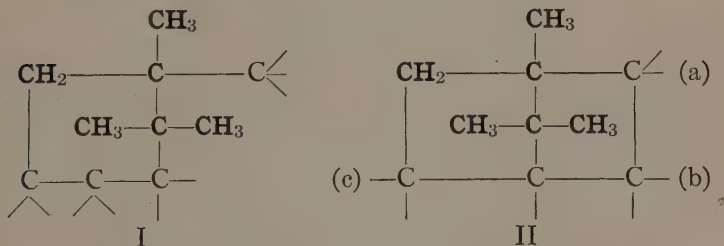
Thus camphor probably contains a ring of six carbon atoms, perhaps a benzene ring, to which two chains of carbon atoms (convertible into $-\text{COOH}$ groups by oxidation) are attached to diagonally *opposite* positions. The problem is to see what these two chains are.

When camphor is oxidized with nitric acid, one of the products is camphoronic acid, which in 1893 was shown to have the structural formula:



In this compound the ring that existed in the original camphor has been broken, and three carboxyl groups, $-\text{COOH}$, have made their appearance. Let us assume that these carboxyl groups occupy the positions that chains or groups of carbon atoms occupied in the missing part of the ring.

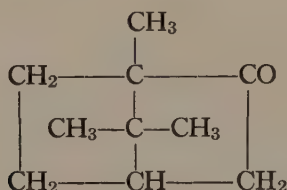
Now if we count the atoms in camphoronic acid that are printed in black type, we get C_6H_{11} ; and comparing this with the molecular formula of camphor, $\text{C}_{10}\text{H}_{16}\text{O}$, we see that we still are short four carbon atoms, which we must put *into the positions of the three carboxyl groups of camphoronic acid*. It is very easy to see that there are only two ways of inserting four carbon atoms in such a way as to get a ring of *six* carbon atoms:



But we must reject I, because it places substituting groups, $-\text{CH}_3$, in neighboring (*ortho*) positions around the ring; whereas the formation of *p*-cymene by distillation of camphor with phosphorus pentoxide (as described above)

requires that the substituting groups be in opposite (*para*) positions. This objection does not apply to II, although II does present the novel feature that one of the two oppositely-placed substituting groups is in reality a bridge across the six-carbon ring.

Our formula still lacks five hydrogen atoms and an oxygen atom. The latter must go in at one of the positions (a) or (b)* to form a ketone group, —CO ; for camphor betrays itself to be a ketone by the fact that it is changed into an alcohol, $\text{C}_{10}\text{H}_{17}\text{OH}$, by vigorous reducing agents. The choice between these two positions depended on a further study of the reactions of camphor, and finally fell upon (a), while the five remaining valence bonds take the five atoms of hydrogen. Thus camphor is a saturated, two-ringed ketone:



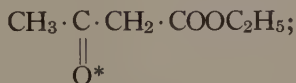
This description hardly gives an idea of the difficulties that beset the workers who struggled with the question of the constitution of camphor during more than a quarter of a century; for here as elsewhere in this book the false steps that have sometimes been taken in the progress of research have been passed over lightly or ignored. Actually, as many as thirty different structural formulas for camphor were seriously proposed, before the weight of accumulating evidence forced the choice that we have made. Its correctness was soon demonstrated, however, by the successful synthesis of camphor from simpler prod-

* The third position (c) is easily seen to be identical with (b), if we imagine the molecule to be rotated about a vertical axis.

ucts, along lines suggested by the formula adopted; and when the structural formulas of the near relatives of camphor had been worked out, the commercial synthesis of camphor itself was made possible from a cheap and plentiful raw material. This was pinene, the chief ingredient of turpentine. Thus natural camphor, a product of the camphor tree, formerly the nearly complete monopoly of Japan, today must meet the competition of synthetic camphor from turpentine. Almost half the 3,000 tons of camphor imported into the United States in 1927 was synthetic camphor.

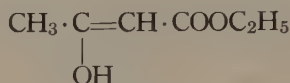
By the middle eighties chemists had come to the conclusion that the atoms that compose any given organic molecule are arranged according to a definite architectural plan. Each hydrogen atom in the molecule was assumed to occupy a definite position; and when any other atom or group was substituted for hydrogen, it was supposed always to enter into the very position that had been occupied by the hydrogen displaced.

Yet this idea of fixed and invariable atomic positions, or rigid molecular architecture, was to receive a rude shock. In 1863, just following the work of Kekulé on the tetravalency of carbon, a colorless liquid was discovered of the formula $C_6H_{10}O_3$. This was *acetoacetic ester*. The manner of its preparation revealed its structural formula, save for one small detail: Certain of the reactions of acetoacetic ester showed it to contain an oxygen atom (here starred) doubly linked to carbon,



I. *Keto form*

but other reactions indicated that it must contain a hydroxyl radical:



II. *Enol form*

Chemists were drawn in, one by one, to champion the one formula or the other, until acetoacetic ester had become the center of the most persistent series of researches and the bitterest controversy that the chemical world had seen since the days of Berzelius, Dumas and Gerhardt. After years of effort the question of its structural formula still remained undecided. Was it possible for one and the same chemical substance to possess two different structural formulas? To grant this seemed to undermine the very foundations on which the structure of organic chemistry had been reared.

Yet as years passed, other substances were discovered with dual personalities. In nearly every instance debate centered around the question of the position occupied by a hydrogen atom. Did it belong in a hydroxyl group, for example, or was it joined directly to carbon? So, little by little, the conviction grew that certain organic substances possess an occasional atom that refuses to "stay put," but wavers between one position and another. In consequence, a sample of any such substance, no matter how carefully purified, behaves as if it were a mixture of two different substances at once.

The final proof that acetoacetic ester is actually such a mixture was obtained in 1911, when it was found that a solution of the substance in an inert solvent deposits crystals at $-78^\circ\text{C}.$, which melt at $-39^\circ\text{C}.$ and have exclusively the characteristics to be expected of the keto form (I). On the contrary, the sodium derivative of acetoacetic ester, when treated with dry hydrogen chloride

gas at very low temperatures, produces a substance with the properties to be expected of the enol form (II).

In 1920 it was also found possible to separate the enol form from the mixture which constitutes ordinary acetoacetic ester, by mere distillation in a vacuum. So simple did the final solution prove to be of a problem with which chemists had struggled for nearly sixty years! At room temperature either the keto or the enol form is in part transformed very slowly into the other form, thus forming a mixture which at length comes to be identical with ordinary acetoacetic ester. We have here a reversible equilibrium between two forms of the same substance:

Keto form \rightleftharpoons Enol form,

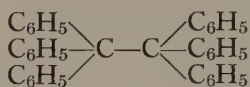
a phenomenon which chemists are pleased to call *dynamic isomerism*.

Proof has been brought that other substances of similar Jekyll and Hyde behavior are also mixtures of such "dynamic isomers," which readily pass from one form into the other. Wavering hydrogen atoms, or indeed wavering groups of atoms, are not at all uncommon. Yet the atoms of the *carbon skeleton* nearly always do remain where they are put; and we have learned to recognize the types of structure that permit other atoms to wander from one point of attachment to another. Thus organic chemistry, which has been reared on the assumption of a rigid molecular architecture, with atoms in definite fixed positions, is unshaken by the discovery that atoms do sometimes shift about within a formula, from one position to another.

And now a second great tenet of organic chemical faith—that carbon must always manifest a valence of four—was to be challenged. In 1900 an American chemist, Gomberg, at the University of Michigan, discovered a colorless crystalline compound that dissolved in most organic sol-

Trivalent
Carbon

vents to form yellow solutions. From the method by which it was prepared, it was expected to possess the formula:



This is the formula of a saturated compound, yet the given substance was apparently unsaturated, since it combined directly with the halogens, hydrogen, oxygen, and even with inert solvents, such as carbon disulfide and chloroform. Moreover, it dissolved in liquid sulfur dioxide to form conducting solutions, which hydrocarbons in general do not do. Finally, some simple relatives of the original compound have been discovered that have only half of the molecular weight that they would possess were they related to the formula given above.

Thus after many years of research the conclusion was reached that the original substance and many of its relatives, represent mixtures of *different forms of the same substance*, as was proved to be the case with acetoacetic ester, with the additional interest in the present instance, that two of the four forms present in the mixture possess a carbon atom with a valence of three.

Occasional other compounds have been observed with trivalent carbon, and a few in which carbon has a valence of two. Thus the two chief assumptions on which structural organic chemistry has been reared—rigid molecular architecture and carbon with a valence of four—have been proved to be not invariably true. Yet the exceptions that have been observed to these rules have proved instructive. Science approaches truth by a series of approximations; and trial conclusions still prove helpful even though they are only generally true. Scientific hypotheses were never meant to be permanent dwelling-places. They are mere landing fields from which the exploring intellect may take off on new flights into the realm of the unknown.

CHAPTER VIII

CHEMISTRY IN SPACE

THREE hundred years ago there was born in Holland one of the great geniuses of science, Christiaan Huyghens.

Huyghens Distinguished at an early age for his mathematical researches, he presently made observations of the greatest importance in physics. He was the inventor of the pendulum clock, and of methods of combining lenses that made possible the modern telescope and microscope. With his improved telescope he first clearly made out the rings of Saturn, and discovered one of Saturn's moons. At the moment he reached the height of his scientific fame, his father, Constantijn Huyghens, was the foremost political figure and the most eminent literary man of the Dutch Republic.

In 1678 Huyghens recorded an observation on light, which two centuries later was to lead to a great advance in organic chemistry. It had often been noted that objects viewed through a crystal of Iceland spar (a form of calcium carbonate) are "seen double." This is because a beam of light, on being passed through such a crystal, is split into two beams, which emerge in slightly different directions. Huyghens found that these two beams could be definitely separated, by a crystal of proper proportions; and when either of these was passed through a second crystal of Iceland spar, the light that got through could be made to wax and wane *merely by rotating the second crystal on its axis*. Indeed, at every half-turn of the crystal no light got through at all!

**Polarized
Light**

This interesting and puzzling phenomenon remained unexplained for a hundred and thirty years. Then a French physicist, Malus, who was pursuing a life of quiet investigation in the midst of the tumult of the Napoleonic Wars, discovered that the two beams of light which issued from the first crystal had some properties which were very different from those of ordinary light. Nevertheless when they were recombined into a single beam, ordinary light was the result.

We now speak of the light of either of the two beams that issues from a crystal of Iceland spar as being "plane

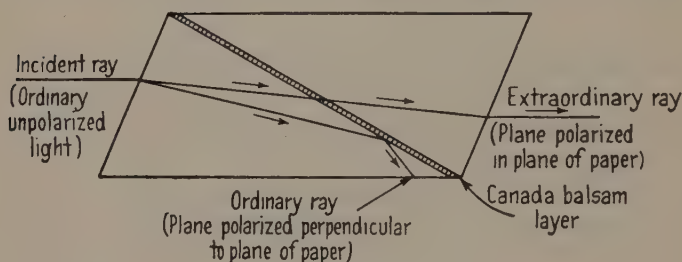


FIG. 1

polarized." We commonly think of it as consisting of vibrations in the ether which are all restricted to a single plane. Ordinary light, by contrast, consists of haphazard vibrations, in all conceivable planes. The effect of a crystal of Iceland spar is to resolve these haphazard vibrations into two sets of vibrations, in planes at right angles to each other. Thus when the two beams that issue from Iceland spar are recombined, ordinary light is obtained.

It is possible to cut a crystal of Iceland spar in a special way to prepare what is called a *Nicol prism* (Fig. 1). This resolves ordinary light into two beams, one of which is absorbed and extinguished; while the other is transmitted as plane polarized light. This is as if a series of waves, sent along a slack rope by moving one end of the rope in haphazard directions, were to meet a vertical

slot in a wall. Evidently only those waves which happened to move in a vertical plane would get through the slot. The rest would all be intercepted at the slot and extinguished; and on the farther side we would have only waves "polarized" to vibrate in a vertical plane.

In the observations of Malus with polarized light it was noted that the plane in which a beam of light is polarized may be twisted, or turned through an angle, by passing the beam through certain crystals. Thus, when a beam that is polarized in a vertical plane (*A*, Fig. 2) is passed through a crystal of quartz, the beam that emerges is polarized in an inclined plane (*B*) that is inclined to the vertical at an angle that depends on the thickness of

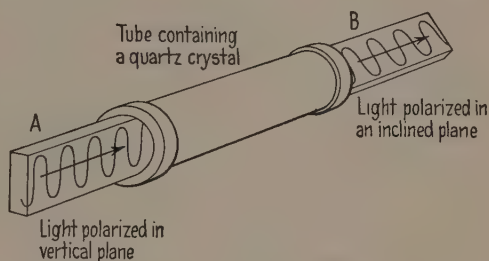


FIG. 2

the crystal, and on the material of which it is composed.

Materials that have a capacity for twisting the plane of polarization of polarized light through an angle are said to be *optically active*. Optically active crystals commonly lose their optical activity when the crystal structure is broken down by melting or dissolving them. They therefore evidently owe their activity to some peculiar manner of arrangement of atoms within the crystal.

Yet there are optically active *liquids*, and many substances form optically active *solutions*. Optically active *vapors*, too, are known. Thus we are compelled to believe that optical activity, for such substances, is a property of the *individual molecule*, and is related to a manner of arrangement of the atoms within the molecule, rather than a manner of arrangement within the crystal as a whole.

There are two sorts of quartz crystals in nature, which we may call right- and left-handed crystals (Fig. 3). In the one variety, the faces which we have labeled *a*, *b*, *c*, *d* are arranged in a clockwise sequence, about one end of the crystal. In the other variety, the same faces are arranged in a counter-clockwise sequence. Human hands present the same difference; for the fingers which the pianist distinguishes as 1, 2, 3, 4, 5 occur on one hand in a clockwise sequence and on the other in a counter-clockwise sequence (Fig. 4). Another way of ex-

Right- and
Left-Handed
Crystals

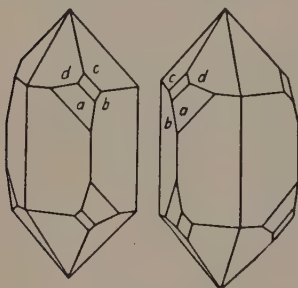


FIG. 3

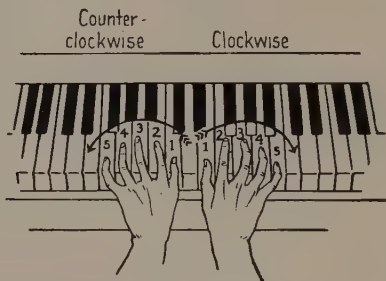


FIG. 4

pressing the same thing is by saying that the two sorts of quartz crystals or the right and left hands are *mirror-images* of each other; that is, each has the appearance that the other would have if viewed in a mirror. After the work of Malus on polarized light it was suspected and confirmed that the two varieties of quartz crystals twist the plane of polarized light by equal amounts, *in opposite directions*. The same has been found to be true of other substances that occur in right- and left-handed crystalline forms.

The Napoleonic Wars were over. Malus and his generation had passed on. Fifty years rolled by—the period that saw the development of organic chemistry from the first accurate organic analyses to definite structural formulas, based on carbon with a valence of four. Then,

from organic chemistry, came a new discovery. Many substances obtained from plants and animals are *optically active* (p. 91)—an observation made by Biot, a pupil of Malus, and the inventor of the polariscope, an instrument by which optical activity may be measured. But as soon as a few examples of these optically active plant and animal products had been synthesized in the laboratory, they were found to be optically *inactive*. This was startling. The organic chemist had proved that many of the compounds of the world of plants and animals may be synthesized without the aid of life. But were there compounds (the optically active compounds), after all, which depended on life or some mysterious “vital force” for their production? Were two substances having the same set of properties, save that one was optically active and the other inactive, to be regarded as identical or different? Here was a problem that challenged attention.

Gradually, the conviction grew that the optically active and inactive forms of a given substance possess not merely the same molecular formula but the same structural formula! The problem grew more intriguing. It seemed plain that the presence or lack of optical activity is due to some difference in structure that ordinary structural formulas cannot express—presumably because they are flat, one-plane affairs, whereas the molecules themselves are built up in three dimensions, in space. An ordinary, one-plane structural formula is to the molecule that it represents as the architectural plan of a building is to the building itself.

Meanwhile a young French chemist, Louis Pasteur, who was a pupil of Biot, and who was destined to become one of the most distinguished scientists of any age, found the clue that was to lead to the solution of the problem of the arrangement of atoms in space. Two different organic

Active and
Inactive
Forms of
the Same
Substance

The Work
of Pasteur

acids may be obtained from grapes, or from the sediment that collects at the bottom of casks of wine. Solutions of one of these, tartaric acid, and solutions of its salts, the tartrates, are optically active. By contrast, racemic acid and its salts, the racemates, form optically inactive solutions. Yet in other respects tartaric and racemic acids appeared to be identical. They had the same percentage composition, the same chemical properties, and formed solutions of the same density and refractive index. Were they identical as well in crystalline form? To settle this question Pasteur evaporated a solution of sodium ammonium racemate, and examined the crystals with a lens.

An unpractised eye would have missed what Pasteur now observed: that the sodium ammonium racemate produced *two sorts of crystals* which were mirror-images of each other. Right- and left-handed crystals again! With a lens and forceps he sorted out the two types, and dissolved them separately. One solution turned the plane of polarization of polarized light toward the right by just the amount that would have been observed had he used the salt of tartaric, instead of that of racemic acid. The other turned the plane of polarization an equal amount toward the left.

It happens that the two sorts of molecules crystallize in separate crystals, when a solution of sodium ammonium racemate is evaporated slowly at room temperature. Pasteur was thus able to separate them with a lens and forceps. But we realize how very easily he might have missed his discovery when we record that if the solution had been evaporated at summer temperature or above, or if certain other salts of racemic acid had been used, a third type of crystal would have been produced, which would have contained equal numbers of both sorts of molecules, and which would have been optically inactive.

Racemic acid, then, is a mixture of equal numbers of right- and left-rotating molecules of tartaric acid. Pasteur suggested (1860) that the right- and left-rotating mole-

Mirror-Image Molecules

cules differed in the arrangement of their atoms in space, and were perhaps to be likened to a right-handed and left-handed screw. A more complete explanation had to await developments made possible by the work of Kekulé.

Then, when carbon had been recognized as possessing a valence of four (p. 56), and when structural formulas had been developed as we write them today, the answer was at hand. Most appropriately, it came from a countryman of Huyghens, who had first observed the phenomenon of polarized light, two hundred years before. This new contributor to chemistry in space was Van't Hoff, who in 1874, at the age of twenty-two, advanced an explanation for the existence of right- and left-rotating *optical isomers* that has stood the test of subsequent experience. Independently a French chemist, Le Bel, arrived at a similar, though less complete, result.

Since carbon has a valence of four, let us represent a carbon atom as occupying the center of a solid with four vertices, commonly called a *tetrahedron* (Fig. 5). At each of the four vertices of the tetrahedron, let us now attach four other univalent atoms or groups corresponding to the four valences of carbon. Thus we have a solid representation of the structural formula of a simple compound, such as methane (Fig. 6) or acetic acid (Fig. 7).

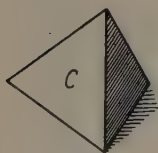


FIG. 5

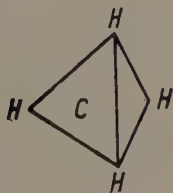


FIG. 6

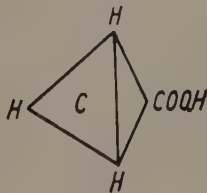
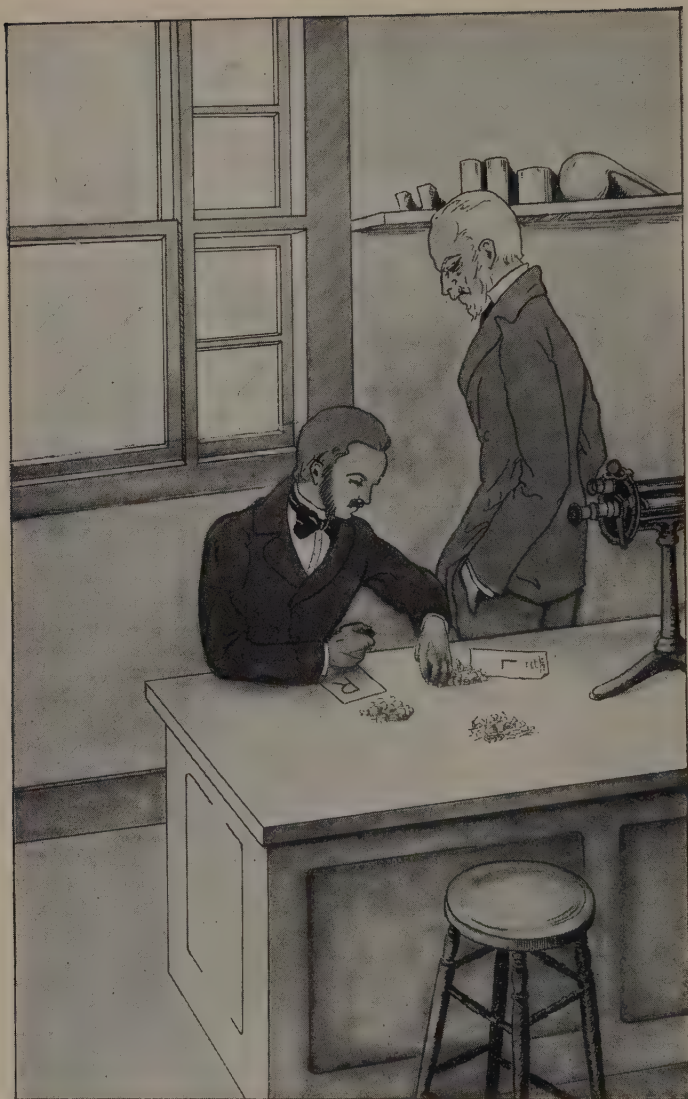


FIG. 7

Next consider Fig. 8. If the four atoms or groups that are attached to a given carbon atom are *all* different,



PASTEUR SORTS CRYSTALS

"M. Biot sent for me to repeat before his eyes the several experiments. He gave me racemic acid which he had himself previously examined and found to be quite inactive to polarised light. I prepared from it in his presence the sodium ammonium double-salt, for which he also desired himself to provide the soda and ammonia. The liquid was set aside for slow evaporation in one of the rooms of his own laboratory, and when 30-40 grams of crystals had separated he again summoned me to the Collège de France, so that I might collect the dextro- and laevo-rotatory crystals before his eyes, and separate them according to their crystallographic character, asking me to repeat the statement that the crystals which I should place on his right hand would cause deviation to the right, and the others to the left. This done, he said that he himself would do the rest. He prepared the carefully weighed solutions, and, at the moment when he was about to examine them in the polarimeter, he again called me into his laboratory. He first put the more interesting solution, which was to cause rotation to the left, into the apparatus. Without making a reading, but already at the first sight of the colour-tints presented by the two halves of the field in the Soleil saccharimeter, he recognised that there was a strong laevo-rotation. Then the illustrious old man, who was visibly moved, seized me by the hand, and said, 'My dear boy, I have loved science so much all my life that that makes my heart flutter.'"—P. F. Frankland, Kekulé Memorial Lecture, *Journal of the Chemical Society (London)* 1897, p. 689.

we may place one of them in the position *a* and then arrange the others (*b*, *c*, *d*) either in a clockwise or in

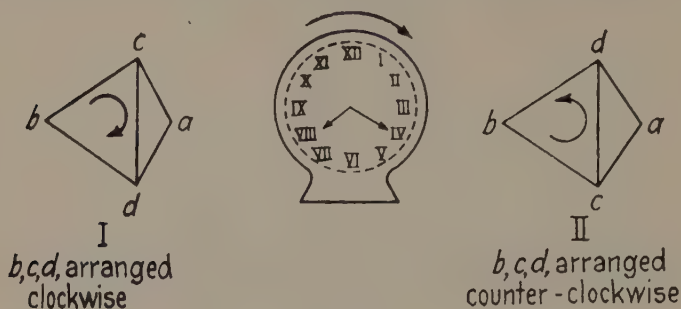


FIG. 8

a counter-clockwise sequence. These two arrangements correspond to two oppositely-rotating optically active

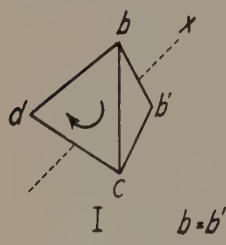
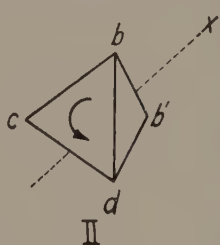
 $b = b'$ 

FIG. 9

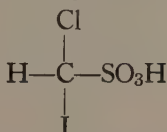
molecules. But when two or more of the four attached atoms or groups are alike ($b = b'$ in Fig. 9), the clockwise and counter-clockwise arrangements of *b*, *c*, *d* are really identical: for merely

by rotating I, Fig. 9, through an angle of 180° , about the axis marked *x*, so that *b'* comes into the position *b*, and *c* into the position *d*, we obtain an arrangement that is identical with II, whenever *b* is identical with *b'*. However, if we try the same thing in Fig. 8, where *a*, *b*, *c*, *d*, are all different, we find that no sort of rotation will transform I into II.

Thus the condition that an organic compound shall exist in two oppositely rotating optical isomers is that it shall contain at least one carbon atom to which four atoms or groups are attached which are *all different*. We call

this an *asymmetric carbon atom*. Whenever such an atom is present, then for every plane formula, two different space formulas are possible, which are mirror-images of each other, and which correspond to the two oppositely rotating forms of the given compound. In illustration, let us refer again to acetic acid, $\text{CH}_3 \cdot \text{COOH}$ (Fig. 7). Since three of the atoms that are attached to the central carbon atom are identical, there is only one form of acetic acid, and this is optically inactive. If these three atoms are made different, as they are in fluor-chlor-brom-acetic acid, $\text{CFCIBr} \cdot \text{COOH}$, then two forms exist, which rotate polarized light equally, in opposite directions.

A simpler compound yet, which contains but a single carbon atom, and that an asymmetric atom, is



It is left to the reader to indicate here the two space-formulas that correspond to this plane formula.

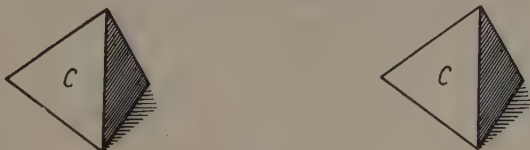


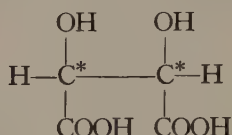
FIG. 10

Any element which possesses a valence of four has the same possibilities as carbon itself. Many optically active compounds have indeed been obtained of lead, tin, germanium and silicon. Nitrogen, with a valence of five, also forms optically active compounds, and cobalt and iron, with a valence of six. The cobalt compounds, in particular, furnish a fine example of how useful a general theory may be in suggesting facts which might otherwise have remained unknown. For a Ger-

Optically
Active
Inorganic
Compounds

man chemist, Werner, in considering the different possible space arrangements of other atoms with respect to a central cobalt atom, was not only led to discover a great new group of optically active inorganic substances, but to predict many of their most interesting properties in advance.

Now let us return to tartaric acid, made famous by the work of Pasteur. It has the formula



We see at once that each of the two central carbon atoms (starred in the formula) is asymmetric, namely, is attached to four atoms or groups which are all different from each other. It may happen that the two asymmetric atoms tend to twist the plane of polarized light in the same direction. The compound is then strongly right-rotating or left-rotating, as the case may be. Or it may happen that the groups arranged about the two asymmetric atoms act in opposite directions. The compound will then be optically inactive.

The Forms of Tartaric Acid

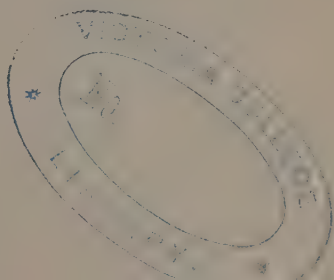
Thus we see that there are three different forms of tartaric acid: right-rotating or *dextro*-tartaric acid; left-rotating or *levo*-tartaric acid; and *inactive* tartaric acid, sometimes called mesotartaric acid. These are commonly referred to as *d*-tartaric, *l*-tartaric, and *i*-tartaric acids. In addition, there is racemic acid, which Pasteur discovered to be composed of equal numbers of molecules of *d*-tartaric and *l*-tartaric acids (p. 94), and which is therefore often termed *dl*-tartaric acid. If a solution containing such a pair of optical opposites is evaporated, the two types of molecules sometimes appear in separate crystals and sometimes in the same crystal.

We have already remarked that when a substance is synthesized in the laboratory from relatively simple, inactive materials, it is always optically inactive, even though the same substance, when produced by living plants and animals, is optically active. The reason is now easy to explain. When reactions take place in test-tubes and beakers the chance of the atoms coming into the arrangement that results in right-rotation is just equal to the chance of their coming into that which results in left-rotation. In consequence, the two types of molecules are formed in equal numbers and the resulting mixture is optically inactive. Such a mixture of equal numbers of molecules of optical opposites is sometimes called a *racemic mixture*, since racemic acid was the first known example of this kind.

Living plants and animals, on the contrary, are principally composed of compounds that are optically active. And working with a mechanism the different parts of which are all definitely right- or left-handed they produce right- or left-handed products, just as a factory produces nuts, bolts and screws with right- or left-handed threads, because of the right- or left-handed bias of the thread-cutting machines. The marvel is not that living plants and animals continue to produce optically active compounds, but how living matter got a right- or left-handed bias in the first place. At present, we have no answer.

Since any attempt to synthesize an optically active compound in the laboratory practically always results in equal numbers of molecules of the *d* and *l* forms (a racemic mixture), we are confronted with the problem of separating these two forms from each other. If the two optically opposite forms happen to crystallize out of a solution in separate crystals, we can sort these by hand, as Pasteur did with the crystals of sodium ammonium racemate.

Pasteur also found that the molecules of the *d*- and



l-forms of an optically active substance could be sorted with the aid of micro-organisms. When a certain green mold was permitted to grow in a solution of ammonium racemate, the solution slowly became levo-rotatory (left-rotating). The mould had destroyed the dextro-rotatory (right-rotating) component of the racemic mixture, leaving the levo-rotatory form behind.

It has since been discovered that the molds and bacteria quite generally attack one form of an optically active substance to the exclusion of the other. Thus, if we have a mixture of the *d*- and *l*-forms of a synthetic sugar it is often an easy matter to find some micro-organism that will ferment the one form and not the other. This suggests again that the chemical mechanism of the micro-organisms, like the thread-cutting machines of our mechanical analogy, has a right- or left-handed bias. A consequence of this right- or left-handed bias of living matter in general is that it often finds one form of an optically active substance poisonous, while the other is almost non-poisonous. We even discover that one form of a substance sometimes tastes sweet, while its optical opposite is tasteless.

Let us imagine equal numbers of right- and left-handed persons to be seated in a lecture room in which all the seats are provided with right-arm tablet rests. The right-handed individuals will be able to write in a normal and comfortable position; but the left-handed ones will be forced to twist around in their seats toward the right. In this attitude they will no longer be mirror-images of their right-handed companions. The two groups will therefore differ in their properties, such as their capacity for observing an announcement posted on the left-hand wall. The right-hand tablet rests automatically sort out and distinguish the right-handed from the left-handed individuals.

By analogy, if we have a mixture of right-handed and

Sorting
Molecules
With the
Help of
Micro-
organisms

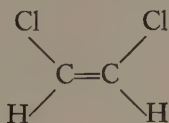
Still Another
Method

left-handed molecules, which we represent by R and L , if we add a second substance, R' , which is itself right-handed, and capable of combining with the former substance, we shall obtain two products, RR' and LR' . These will be very different in all their important properties, and may readily be separated by taking advantage of their different solubilities in some solvent. This is the most convenient and the most famous of the methods that have been proposed for separating optically inactive mixtures into their right-handed and left-handed components.

At present, then, optical activity in the non-crystalline realm is exclusively the result of life. Either we must have the constructive activity of living plants or animals, the destructive activity of living micro-organisms, or the selective activity of a living human brain, in planning a chemical combination with an optically active reagent and in directing the course of a crystallization.

When Van't Hoff published his famous essay, "Chemistry in Space," in 1875, he was not only able to explain the optical activity of organic compounds in terms of the asymmetric carbon atom, but to predict some interesting new relationships. Let us consider a compound containing a double bond between two neighboring carbon atoms:

Atoms
Spaced Near
and Far



In space, the double bond would be represented by placing *two* corners of one carbon tetrahedron in contact with *two* corners of the other (Fig. 11, p. 104).

Thus we see that the one plane formula corresponds to two different space formulas. In one of these (*I*) the two chlorine atoms are on *the same side* of the carbon atoms, and in the other (*II*) they are on *opposite sides*.

This anticipation has been fully confirmed. Whenever we have a double bond, linking two carbon atoms, each of which is connected to two *different* atoms or groups, two different space formulas are possible. In nearly every instance, two corresponding compounds have been prepared; though it sometimes happens that one of the compounds to be expected cannot be produced, apparently because there is sometimes too little space to accommodate two large or complicated groups on the same side of the doubly linked carbon atoms.

These considerations are often of practical importance in synthesizing organic compounds, since reactions that would otherwise be expected sometimes fail to take place, for lack of space in which to effect an interchange or

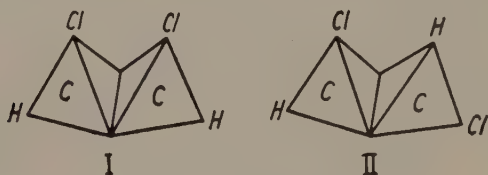


FIG. 11

rearrangement of groups. As we learn more about the subject we may find that hindrance or lack of hindrance to chemical reactivity, according as groups of atoms are spaced near together or far apart, is perhaps the reason that a given organic compound is often highly toxic to living organisms, though a closely related compound may be almost non-toxic. Thus so abstract and theoretical a topic as the arrangement of atoms in space has led to useful results that could have been obtained in no other way. Chemical science makes progress, not by hasty forays bent on seizing results of immediate utility, but by a patient exploration of the universe of the infinitely small, beyond the fields traversed by our heavy-footed human senses.

PART II

THE ORGANIC CHEMICAL INDUSTRIES

CHAPTER IX

SYNTHETIC METHODS

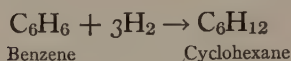
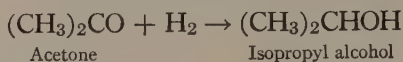
WE have related the story of the way in which organic chemistry progressed to the stage in which structural formulas were known. During the decades that were required for these advances, great progress was made in synthesis. Indeed, progress in knowledge of structural formulas and progress in synthesis are inseparable. In the earlier years of the science, a few organic compounds were discovered by hit-and-miss trial of reagents. At present, synthesis is based on structure. The structural formula, itself perhaps derived by years of preliminary effort, is made to serve as an architect's plan to guide the chemical workman, as he builds a complex molecule, atom by atom, from simpler molecules. To understand the achievements of the organic chemist in duplicating Nature's products and in creating products unknown in Nature, we must learn something about his experimental devices—chemical "tricks of the trade"—as illustrated by some famous methods of synthesis.

One of the simplest of the expedients of synthetic chemistry, though actually one of the latest to be developed, is *hydrogenation*—the direct addition of hydrogen to an organic compound. Theoretically, any of the unsaturated compounds, which are characterized by their capacity for combining directly with chlorine or bromine (p. 63), ought to combine directly with hydrogen as well. In practice, it is not so easy to make them do it.

Hydrogena-
tion

A beginning was made by a French chemist, Paul

Sabatier, who demonstrated (about 1907) that the *vapors* of a great many compounds will combine directly with hydrogen when a mixture of the vapor and hydrogen gas is passed over finely powdered metallic nickel, at temperatures near $400^{\circ}\text{C}.$:



The nickel itself suffers no apparent change. It merely serves as a *catalyzer*—a name given to any material that speeds up a chemical reaction without itself being permanently altered.

Next it was discovered that a catalyzer of very finely powdered platinum or palladium will enable many organic *liquids* to be hydrogenated. Finally, means were found for producing finely powdered nickel of sufficient catalytic activity to cause unsaturated vegetable oils and unsaturated fatty acids to combine directly with hydrogen. In this way liquid oils, which are mostly unsaturated compounds, are converted into saturated solid fats. Cocoanut and cottonseed oils are now transformed on a large scale into solid lard substitutes (p. 215). Whale oil and fish oils are hardened, and at the same time are deprived of objectionable odors, and thus become available for the manufacture of soap.

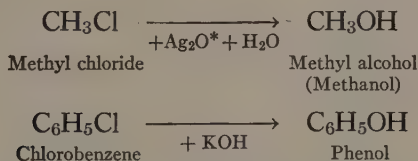
In commercial practice the principal difficulties to be overcome were in securing a sufficiently cheap method for producing hydrogen, and in preventing the nickel catalyst from being rendered inactive by the presence of traces of impurities in the hydrogen and oil. A great many patents were taken out in Europe and America, which gradually resulted in a great industry that now produces several hundred thousand tons of hardened fats each year. Sabatier, whose patient researches laid the foundation for

these industrial developments, did not himself participate in their rewards; though he made a tour of the United States in 1927, at the expense of a corporation which had benefited by his work.

SUBSTITUTION

Dumas discovered one of the most useful of organic reactions when he observed the action of chlorine on organic compounds. If an unsaturated compound is treated with chlorine, the latter adds itself directly; a saturated compound, however, usually has a part of its hydrogen atoms *replaced* by chlorine—a process that we know as substitution (p. 48). Long experience has taught us where the chlorine atoms go, when they are added directly to an unsaturated compound or when they replace hydrogen in a saturated one. That is, we know from the structural formula of the original compound just where the chlorine atoms are to be expected in the structural formula of the “chlorinated” product. Then, by replacing chlorine by oxygen or hydroxyl we can obtain other products still, of known structural formulas.

A common expedient is to treat the chlorinated compound with moist silver oxide, or in some instances with potassium hydroxide; or even with water, at high temperatures. A single chlorine atom is thus replaced by hydroxyl; or a pair of chlorine atoms (attached to the same carbon atom) is replaced by an oxygen atom:



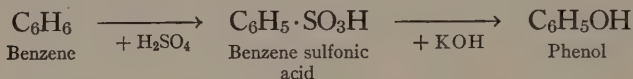
* Here we have written Ag_2O and H_2O inconspicuously beneath the arrow, in the formulation, in order to center attention on the two organic compounds which are converted, the one into the other.

The chlorinated hydrocarbons themselves (CCl_4 , $\text{C}_2\text{H}_2\text{Cl}_4$, and so forth) are important solvents for waxes, fats and oils, and are replacing gasoline in dry cleaning, because they are non-inflammable. Methyl chloride, CH_3Cl , and ethyl chloride, $\text{C}_2\text{H}_5\text{Cl}$, are volatile liquids, which are used in small automatic refrigeration systems.

The aromatic hydrocarbons, such as benzene and naphthalene, may be transformed into oxygen compounds in the manner that has just been described.

Sulfonation

But there are other ways. If we heat an aromatic hydrocarbon with concentrated sulfuric acid, one or more hydrogen atoms are replaced by $-\text{SO}_3\text{H}$ groups, and we obtain a sulfonic acid. This is *sulfonation*. Then by fusing the sulfonic acid with potassium hydroxide, we cause the sulfonic acid groups to be replaced by hydroxyl groups:



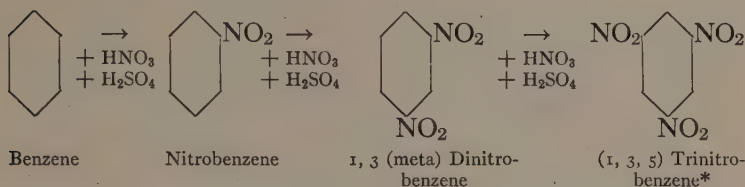
In this way benzene may be transformed into phenol, $\text{C}_6\text{H}_5\text{OH}$; naphthalene, C_{10}H_8 , into naphthol, $\text{C}_{10}\text{H}_7\text{OH}$; and so forth. Or several hydrogen atoms of the original hydrocarbon may thus be replaced by sulfonic acid groups, and these in turn by hydroxyl groups, giving such compounds as resorcinol, $\text{C}_6\text{H}_4(\text{OH})_2$, or phloroglucinol, $\text{C}_6\text{H}_3(\text{OH})_3$. Thus a great many substances are brought into being which may be used in the manufacture of dyes. Their source is the aromatic hydrocarbons, benzene, naphthalene, and anthracene, which in their turn are derived from coal (p. 146).

Nitric acid acts on aromatic compounds even more readily than sulfuric acid does, replacing one or more hydrogen atoms by nitro-groups, $-\text{NO}_2$.

Nitration

This is *nitration*. Generally a mixture of nitric and sulfuric acids is used. Thus, according to the temperature and the time that the nitrating mixture acts,

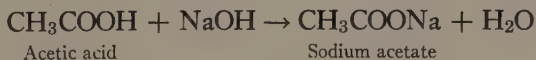
one, two or three hydrogen atoms of benzene may be replaced by nitro-groups:



Having thus introduced nitro-groups into various positions round the benzene ring, we may convert them into amino-groups, —NH_2 , then into hydroxyl groups, —OH . By roundabout methods the hydroxyl groups may be replaced by chlorine, or cyanogen groups, —CN , or carboxyl groups, —COOH ; and all these will usually go into the very positions around the benzene ring that were originally occupied by the nitro-groups.

Sulfonation and nitration, then, are the means by which we contrive to get all sorts of groups into specified positions around the benzene ring. A knowledge of the actual positions occupied by the substituting groups is important, since it determines, for example, whether a dye shall be one color or another, or whether a synthetic medicine shall produce a given effect or one quite different.

The organic acids all contain one or more carboxyl groups, —COOH . It is the hydrogen of this group which is replaced by metals, to form salts:



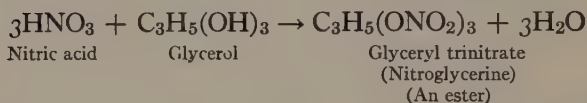
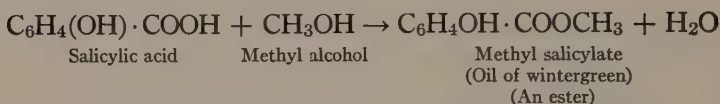
A substance containing one or more hydroxyl groups, united with a non-aromatic radical, is called an *alcohol*;

* The figures refer to the positions occupied by the nitro-groups, numbered in order round the benzene ring.

one containing one or more hydroxyl groups, united with an aromatic radical, is called a *phenol*:

$\text{C}_2\text{H}_5\text{OH}$	$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{OH}$	$\text{C}_6\text{H}_5\text{OH}$	$\text{C}_6\text{H}_4(\text{OH})_2$
Ethyl alcohol (Ethanol)	Benzyl alcohol	Common phenol	Resorcinol
Alcohols		Phenols	

Organic and inorganic acids alike react with the alcohols and phenols to form substances called *esters*. The process is called *esterification*:



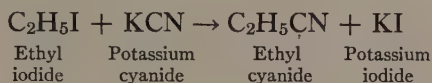
Many of the simplest esters are liquids of pleasant odor, responsible for the fragrance of fruit. Certain perfumes owe their odor largely to esters, usually in admixture with fragrant hydrocarbons, with smaller amounts of other substances (p. 154). Animal and vegetable fats and oils are esters. Other esters are important solvents, used in the preparation of lacquers (p. 186).

CONDENSATION

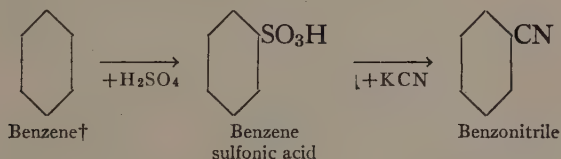
In a former chapter (p. 60) we noted that each molecule of an organic compound may be considered as consisting of a skeleton or framework of carbon atoms, carrying other sorts of atoms in specified positions. We have just seen how the hydrogen atoms that are attached to this framework may be replaced by other sorts of atoms or groups of atoms. The question still remains how we may build additions to the framework itself. This process is called *condensation*. Of the many methods that are used we shall mention only five.

When certain classes of compounds containing chlorine, bromine, or iodine are heated with potassium cyanide, the halogen is replaced by the cyanogen radical, $-\text{CN}$. Thus an extra carbon is added at the previous carbon skeleton, at the point which the halogen* atom previously occupied.

Cyanide
Synthesis

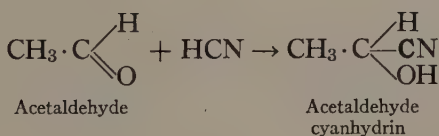


The organic cyanides, thus produced, are generally called nitriles. Aromatic cyanides may similarly be made from sulfonic acid salts, and thus indirectly from the aromatic hydrocarbons, such as benzene.



In this way cyanogen groups may be attached at specified positions around the benzene ring.

Still another class of organic cyanides may be made by direct addition of hydrogen cyanide to an aldehyde:

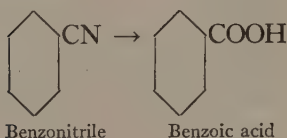
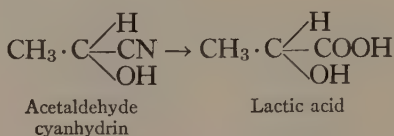


Here we have attached a cyanogen group and therefore an extra carbon atom, shown in bold-faced type, at the end of a chain of atoms.

* *Halogen*, a general term, meaning fluorine, chlorine, bromine, or iodine.

† A hydrogen atom, not shown in these formulas, is attached to each unoccupied corner of the benzene ring (p. 69).

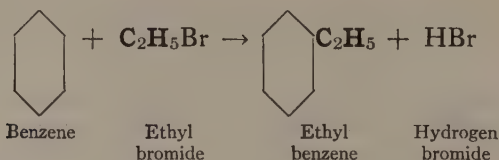
Organic cyanides of all classes combine readily with a number of other sorts of organic compounds. Thus very complicated structures may be built up. Of especial usefulness is the fact that the organic cyanides may be converted into organic acids or salts of organic acids by heating with water or an alkali.



Observe that a cyanogen group, —CN, in each case, is converted into a carboxyl group, —COOH.

In what just precedes we had to be content to attach a single carbon atom at a particular point in a carbon skeleton. Methods have been discovered for attaching a whole group of carbon atoms to the original carbon skeleton, in a single step. In 1881, Friedel and Crafts discovered that such a group of carbon atoms (given in bold-faced type in the following example) may be attached to a benzene ring by heating a compound containing the ring with one containing the group plus chlorine or bromine, using anhydrous * aluminum chloride as a catalyzer.

Friedel-
Crafts
Reaction



* *Anhydrous*, free from water.

By continuing the action with an excess of ethyl bromide we may attach ethyl groups at more than one corner of the benzene ring, or perhaps at all corners; though it must be admitted that we meet with difficulties in the later stages of the process, and may perhaps obtain such a complicated mixture that it is impossible to separate the individual products in a reasonably pure form.

We may begin with any one of a great number of aromatic hydrocarbons, instead of with benzene, and replace one or more hydrogen atoms by a corresponding number of branched or unbranched hydrocarbon chains. Scores of different hydrocarbons of rather complex structure may thus be made directly from comparatively simple aromatic hydrocarbons, produced from coal tar. If we treat these products further by chlorination, nitration, sulfonation, and so forth, as described in the early part of this chapter, we may arrive in the end at the synthetic dyestuffs. Their varied hues are due in a very large degree to the possibility of modifying the structure of the coal tar hydrocarbons from which they are derived, by adding specified hydrocarbon radicals at specified points round the benzene ring.

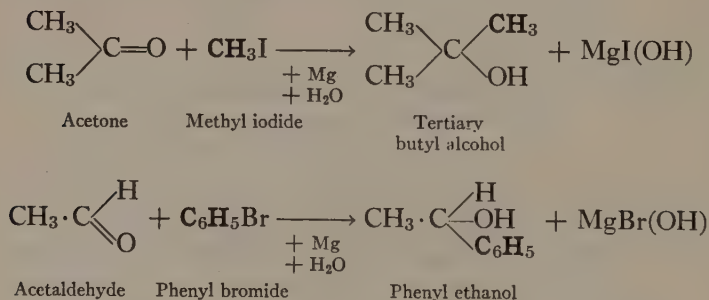
In 1901 a French chemist, Grignard, discovered that when finely divided metallic magnesium is placed in a solution of an organic chloride, bromide or iodide, in ether, the metal rapidly dissolves. The product, which may be recovered as a white solid by evaporating the solution, proved to possess extraordinary chemical activity. It was found to react with aldehydes, ketones, acid chlorides, esters, and still other classes of organic compounds, forming products of the most varied nature.

The synthetic possibilities of these organic magnesium compounds are still further increased by the fact that the original material, brought into contact with magnesium, may be a compound of either the aliphatic or aromatic group. Investigators naturally turned to this method with

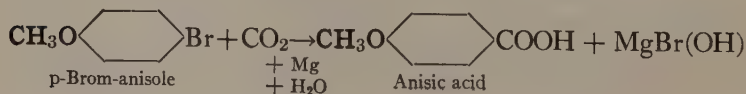
Grignard Syntheses

enthusiasm. A great many researches were published, based on Grignard's discovery, in the years that followed, and each year adds many more. Hundreds of compounds have been produced that were previously unknown. No other synthetic method in the whole realm of organic chemistry approaches the Grignard procedure in versatility.

To illustrate the method, note that we bring the organic substance—whose carbon skeleton is to receive an additional hydrocarbon group—into the presence of a halogen compound which contains that group. At least a small amount of ether or some other substance capable of acting as a catalyzer for the Grignard reaction must also be present. Then, when we add finely divided metallic magnesium, a succession of reactions takes place. In the end, the specified hydrocarbon radical (in bold-faced type in the following examples) is found attached to some point of the carbon skeleton, and the halogen is in combination with the magnesium.

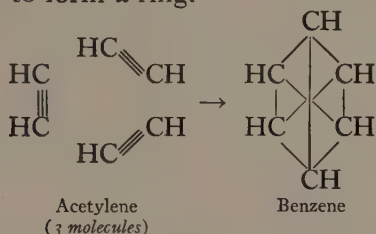


It is interesting to notice that hydrocarbon radicals may be added directly to carbon dioxide by means of Grignard's reaction, forming organic acids.



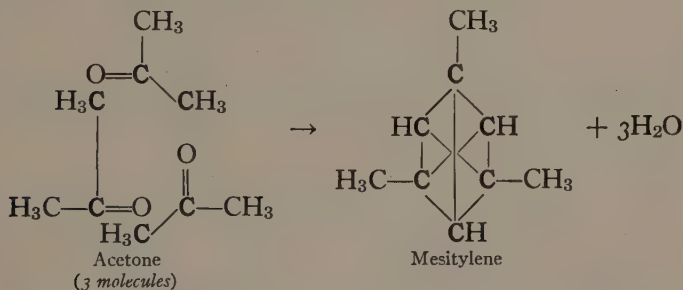
Several molecules of an unsaturated compound sometimes combine with each other. When acetylene, $\text{HC}\equiv\text{CH}$, is passed through a hot tube it is in part decomposed into carbon and hydrogen, and in part condensed to form benzene. In this reaction, three molecules of acetylene are linked up to form a ring.

Ring
Closing

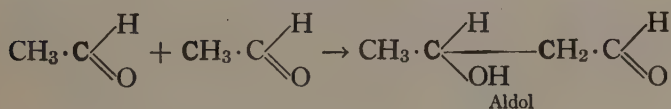


An example of the formation of a ring by the direct union of two molecules of an unsaturated compound is given on (p. 211).

A saturated aliphatic compound may often condense to form an aromatic ring compound, together with water, ammonia, or some other simple product. Thus acetone (CH_3)₂CO, in the presence of dilute sulfuric acid, forms mesitylene (trimethyl benzene).



When acetaldehyde is heated with dilute alkali it is converted into an aldehyde-alcohol, called aldol:



In this reaction the two carbon atoms here shown in bold-faced type have become linked with each other, and

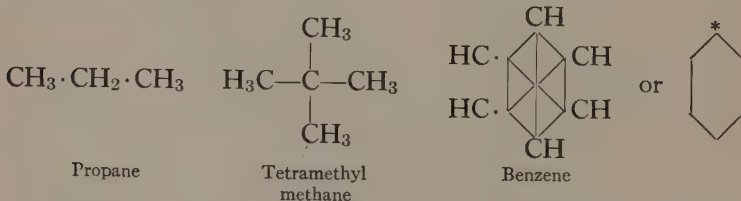
Aldol we have a chain of four carbon atoms where we formerly had but two. We may

repeat the process, using a further quantity of aldehyde, and so produce a chain of six or more carbon atoms. Or we may cause two different aldehydes to condense with each other, or two different ketones, or an aldehyde and a ketone, to give a compound with a lengthened chain of carbon atoms. This is presumed to be the type of synthesis by which plants build up the aldehyde-alcohols and related compounds that we call sugars. In the laboratory its usefulness is limited by the fact that there are other ways in which several molecules of an aldehyde may combine with each other under the influence of alkalies. We are apt to get a complicated mixture instead of a pure product, or even a resin of indefinite composition, without useful properties.

For purposes of reference a few of the main classes of organic compounds mentioned in this and later chapters are here listed, together with their characteristic radicals.

Classes of Compounds

Hydrocarbons contain only carbon and hydrogen. They are either of the aliphatic type (open chains of carbon atoms) or aromatic type (benzene rings), (p. 68).

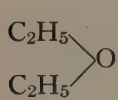


Alcohols contain the group —OH in combination with an aliphatic radical. *Phenols* contain the group —OH ,

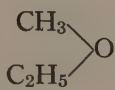
* This shortened formula for benzene is explained on page 69.

in combination with a benzene ring. Examples on page 112.

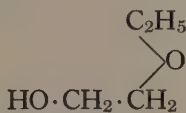
Ethers contain an oxygen atom, >O , linked to two hydrocarbon radicals, which may be identical or different.



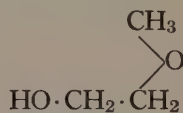
Ethyl
(ordinary) ether



Methyl ethyl
ether

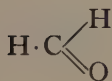


Ethyl glycol ether
"Cellosolve"

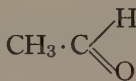


Methyl glycol ether
"Methyl Cellosolve"

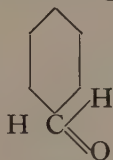
Aldehydes contain the group $\text{—C} \begin{array}{l} \text{H} \\ \diagup \\ \text{O} \end{array}$.



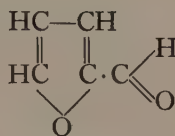
Formaldehyde



Acetaldehyde



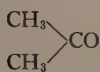
Benzaldehyde



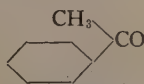
Furfural

Ketones contain the group >CO , in combination with

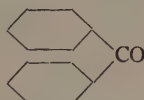
two hydrocarbon radicals, which may be identical or different:



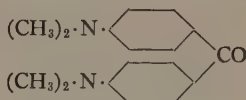
Acetone



Methyl-phenyl
ketone
(acetophenone)



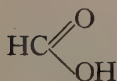
Benzophenone



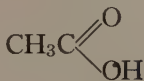
Michler's ketone

Acids contain one or more carboxyl groups, $\text{—C} \begin{array}{l} \text{O} \\ \diagup \\ \text{OH} \end{array}$,

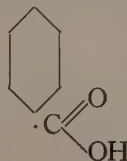
which we have previously written —COOH :



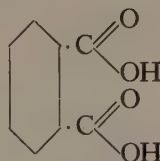
Formic acid



Acetic acid

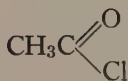


Benzoic acid

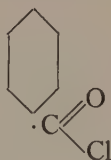


Phthalic acid

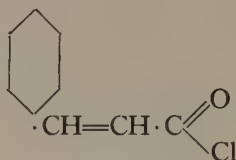
Acid chlorides contain the group $\text{—C} \begin{smallmatrix} \text{O} \\ \text{//} \\ \text{Cl} \end{smallmatrix}$.



Acetyl chloride

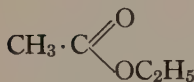


Benzoyl chloride

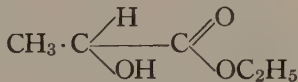


Cinnamyl chloride

Esters contain the group $\text{—C} \begin{smallmatrix} \text{O} \\ \text{//} \\ \text{OR} \end{smallmatrix}$, in which R is a hydrocarbon radical:



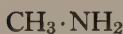
Ethyl acetate



Ethyl lactate

Methyl salicylate
(Oil of wintergreen)

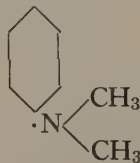
Primary amines contain the group —NH_2 , connected with a hydrocarbon radical; *secondary amines*, the group >NH , with two radicals; *tertiary amines*, >N , with three radicals.



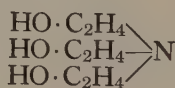
Methyl amine



Aniline

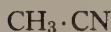


Dimethyl aniline



Triethanolamine

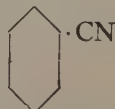
Nitriles or cyanides contain the group —CN :



Acetonitrile



Propionitrile



Benzonitrile

Many compounds contain several groups of a given kind. The poly-alcohols contain several —OH groups in a molecule; * the poly-carboxylic acids, several $\text{—C}\begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{OH} \end{smallmatrix}$ groups, and so forth. Or a compound may contain groups of atoms that place it in several different classes of organic compounds at once. Thus cellosolve and methyl cellosolve, listed under *ethers* above, are at once ethers and alcohols, since they contain both >O and —OH .

* Glycerol, for example, p. 58.

CHAPTER X

CALCIUM CARBIDE PRODUCTS

IN 1862, Wöhler prepared a zinc-calcium alloy, in an electric furnace, using a current drawn from a battery of 200 zinc-carbon cells. At that time there were no electric dynamos. When his alloy was heated with charcoal, the product was a dark mass, which decomposed when thrown into water, liberating a combustible gas. This was the discovery of calcium carbide and acetylene, which are now raw materials for the most far-reaching chemical industries, that make Wöhler's earlier and more famous synthesis of urea (p. 40) seem but a slight accomplishment. Wöhler might have followed up his discovery of acetylene with researches leading to the most important results in organic chemistry. Instead, he was diverted to the inorganic field, and the development of the synthetic possibilities of calcium carbide had to wait thirty years.

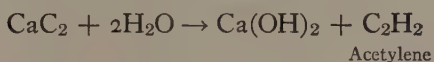
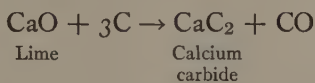
Wöhler
Discovers
Calcium
Carbide

ACETYLENE

IN 1892, a Canadian electrical engineer, Thomas Willson, attempted to prepare aluminum by the reaction of aluminum oxide with metallic calcium. This was before the electrochemical preparation of aluminum had become the established method that it is today. As an incident to the preparation of aluminum in a small plant in North Carolina, Willson attempted to prepare metallic calcium by heating lime with carbon. The result was a brittle, dark-

Thomas
Willson

colored mass, which was discarded as worthless. That day it happened to rain, and a workman lighting his pipe threw the match onto the pile of waste material from the furnace, which immediately caught fire in a most spectacular way. By this accident, thirty years after the discovery of calcium carbide and acetylene by Wöhler, these substances were again brought to the attention of chemists, and were presently produced on a commercial scale.



It was the day of the bicycle. Acetylene bicycle lamps appeared on a thousand highways, and more than one home was wrecked by the explosion of a gas generator in which acetylene was prepared for a household lighting system by the interaction of calcium carbide and water. The first calcium carbide produced was contaminated with calcium phosphide, which gave rise to a spontaneously inflammable gas, phosphine; acetylene, moreover, reacts with copper and some other metals to form dangerously explosive compounds. Furthermore, it is decomposed explosively into its elements, carbon and hydrogen, by an electric spark or by heat, especially when it is highly compressed. Indeed, Willson himself just escaped being killed by the violent explosion of a cylinder in which acetylene had been liquefied in quantity for perhaps the first time.

As an illuminant, then, acetylene was not an immediate success, although methods for preparing purer and safer acetylene were later developed, and in time a safe means was found for its use, in a solution of acetylene in acetone, instead of the compressed or liquefied gas. Willson sold his American patents and returned to Canada, where he de-

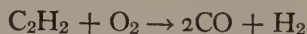
Acetylene
Illumination

veloped other electrochemical products. Hydro-electric power was developed at Niagara Falls in 1895, and the manufacture of calcium carbide there, in electric furnaces, was soon a well-established industry.

During all the years that have since elapsed, acetylene has had to meet the competition of the vigorously expanding electric light industry. Yet even today, in remote parts of this continent, small towns are lighted by acetylene; and acetylene plants are found on many farms. When burned with a special burner, acetylene gives a more brilliant light than any other gas. Lightbuoys and lighthouses are often equipped with acetylene lights that are automatically switched on when the sun sets or is obscured by fog. Airports are frequently equipped with acetylene beacons.

The use of acetylene as an illuminant is, however, quite overshadowed by its use in the oxy-acetylene torch, for welding and cutting metals. It is commonly burned with a volume of oxygen only slightly exceeding that of the acetylene itself, so that the primary products of the combustion are largely carbon monoxide and hydrogen:

**Acetylene
Welding**



Under such conditions a reducing flame is produced, suitable for welding. In cutting steel, the metal is set on fire with the oxy-acetylene flame, then burned away in a stream of oxygen.

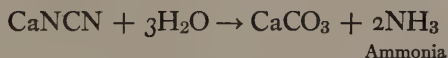
Oxy-acetylene welding is now a great industry, using the chief part of the more than 500,000,000 cu. ft. of acetylene, which the United States produces each year. Automatic welding machines have been developed that are provided with as many as twenty flame tips, burning altogether as much as one hundred cubic feet of acetylene an hour, and welding light-gage metal at speeds of ten or twelve feet a minute. Welding by acetylene or the

electric arc riveting in the construction of steel frameworks for buildings, bridges and even ships.

CALCIUM CYANAMIDE

Chance once more played an important rôle in the development of the calcium carbide industry, in the year 1898. A great rush was on for the gold fields of the Klondike. Gold was produced at a rate never known in the previous history of the world. The new cyanide process for the extraction of gold from its ores came into prominence. Thus the attention of the chemists of the world was directed to the problem of preparing cheap cyanide.

A possible method seemed to be a direct union of nitrogen with calcium carbide to form calcium cyanide, $\text{Ca}(\text{CN})_2$, at the temperature of the electric furnace. When this was tried, the result was not calcium cyanide at all, but a new material, calcium cyanamide, which in purer form is a definite compound, CaNCN , and which was presently to become the most important of the chemical products produced from calcium carbide. For calcium cyanamide is slowly decomposable by water, and more rapidly by steam, producing ammonia:



Ammonia

Ammonia is one of the most important inorganic compounds, for it enters the refrigeration industry as liquid ammonia, the dry cell industry as ammonium chloride, and the fertilizer industry as ammonium sulfate. Several million tons are produced each year.

Calcium cyanamide, applied directly to the soil under proper conditions is a fertilizer, too, furnishing nitrogen for growing crops. The hope to produce gold cheaply by producing cheap cyanide resulted in calcium cyanamide, namely, a means for increasing the world's production

of food. Increased production of gold by the cyanide method would not have saved the world from starvation; calcium cyanamide removed that danger forever.

In the end, numerous other products were obtained from calcium cyanamide. It is easily converted into urea, $\text{CO}(\text{NH}_2)_2$, which Wöhler first synthesized in 1828. Urea is now an important industrial product, synthesized by several different methods. It finds application as a stabilizer for explosives, and in the manufacture of synthetic plastics (p. 198). Under proper conditions it may be used as a fertilizer. From urea, guanidine, $\text{HN}=\text{C}(\text{NH}_2)_2$, and its derivatives may be prepared. Some of these are important accelerators in the vulcanizing process for rubber (p. 209). By fusing calcium cyanamide with soda and coke, it is converted into sodium cyanide, from which Prussian blue, yellow prussiate of potash, hydrocyanic acid, cyanides, and cyanates in general may be made. Thus calcium carbide did finally result in a practical method for the cheap production of cyanides, but not in the direct way that the early investigators hoped.

PRODUCTS DERIVED FROM ACETYLENE PLUS WATER

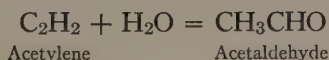
The calcium carbide industry, with its production of acetylene and calcium cyanamide, was assured of a constantly increasing commercial success, from about 1909 onward. The World War came on, with an enormous increase in the demand for acetone, which is used as a solvent in the production of smokeless powder. Presently acetic acid and acetic anhydride were demanded in great quantities, for the production of cellulose acetate lacquers for airplane fabrics. There was an immediate search for new methods of production of these compounds.

Research workers in Canada, France and Germany in-

dependently developed practical methods that made possible the production, on a large scale, of the three substances from calcium carbide. The Canadian plant got into operation within nine months from the time the first laboratory experiments were begun. The following year it produced over 1200 tons of acetone and 10,000 tons of acetic acid. German plants, the same year, had a production of about 7000 tons of acetone, and those in France one of the same order.

In principle, these syntheses of acetic acid and acetone are very simple. In practice a great deal of trouble was experienced. Difficulties were met in the fact that the catalyzers employed were frequently rendered inactive by impurities in the acetylene. There was also constant hazard of explosions, when acetylene research was being pushed forward into unexplored fields. Yet very quickly, under the pressure of military need, these difficulties were overcome.

The first step of the synthesis was the direct union of acetylene with water in the presence of a solution containing a mercury salt as a catalyzer. The result is acetaldehyde:



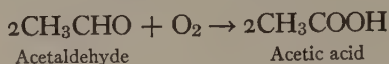
Acetylene

Acetaldehyde

Acetaldehyde itself has many important uses, but its chief interest at the moment of its first commercial production was as an intermediate in the synthesis of acetic acid.

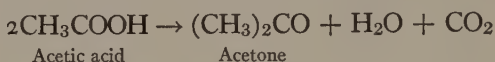
To pass from acetaldehyde to acetic acid, it is only necessary to pass air through the aldehyde, in the presence of a catalyzer consisting of vanadium oxide, cerium oxide, or manganese acetate. The reaction is almost quantitative, and the acetic acid produced by redistillation is over 99 per cent pure. It is interesting to note that the oxygen of the air that is used in this process is practically completely absorbed. The gases escaping from the reaction vessel consist almost completely of moist nitrogen,

which may be used to supplement nitrogen produced from liquid air for the production of calcium cyanamide.



Acetic acid was in such great demand during the war that it might profitably be produced in this way. In normal times, a cheaper source of the acid is found in the destructive distillation of wood (p. 219), or the oxidation of alcohol under the influence of bacteria (p. 265).

It was found possible to make acetone from acetic acid by passing acetic acid vapors over lime in a hot tube.



Most of the acetone of commerce is still produced by a closely related method, the destructive distillation of calcium acetate, which is itself an indirect product of the destructive distillation of wood. We may recall that acetone was thus produced in the Middle Ages, from lead acetate (p. 34). From acetic acid may be derived many other important products, such as acetamide, acetyl chloride, chloroacetic acid, and acetonitrile, which are starting points for still other syntheses (p. 131).

Acetic acid and acetone are but the beginning of the synthetic possibilities of acetaldehyde. In the presence of alkalis it forms aldol (p. 117), which is a useful solvent and is the starting point of one of several known syntheses of rubber. If there were no cheaper way, we could actually produce a fair grade of rubber commercially from calcium carbide by way of acetylene and acetaldehyde. Acetaldehyde and acetic acid may also be readily converted into acetic anhydride, which is essential not only for the production of airplane lacquers, but for all the manifold products that are made from cellulose acetate (p. 188).

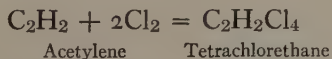
**Aldol and
Acetic
Anhydride**

OTHER SYNTHESSES BASED ON ACETYLENE

Now let us return to acetylene and note some products that may be derived from it by reactions other than those that begin with the direct addition of water, to form acetaldehyde. Acetylene combines directly with nitrogen, under the influence of an electric discharge or ultra-violet light, to form hydrocyanic acid, from which cyanides and numerous other important compounds may be prepared. It combines directly with hydrogen in the presence of catalyzers, to produce ethylene, C_2H_4 , and ethane, C_2H_6 .

Ethylene may be converted indirectly into alcohol, and thus into numerous substances derivable from alcohol. It may also be converted into glycol, $C_2H_4(OH)_2$, which is now coming into use as a substitute for denatured alcohol as an "anti-freeze" in automobile radiators, and which may readily be converted into important solvents for cellulose nitrate and acetate. Thus the solution in an automobile radiator, the lacquer on the hood and body, and the acetate rayon worn by the lady who drives the car are all produced with the aid of compounds that are derivable from calcium carbide.

Other interesting syntheses, starting with calcium carbide, are based upon its capacity for combining directly with chlorine to form tetrachlorethane:



This looks simple enough on paper. In practice much investigation was needed to make it safe. If acetylene and chlorine are brought together in any ill-considered way the result is not tetrachlorethane but an explosion.

Chlorinated
Acetylene
Products

Tetrachlorethane is an important constituent of many of the solvent mixtures that are used

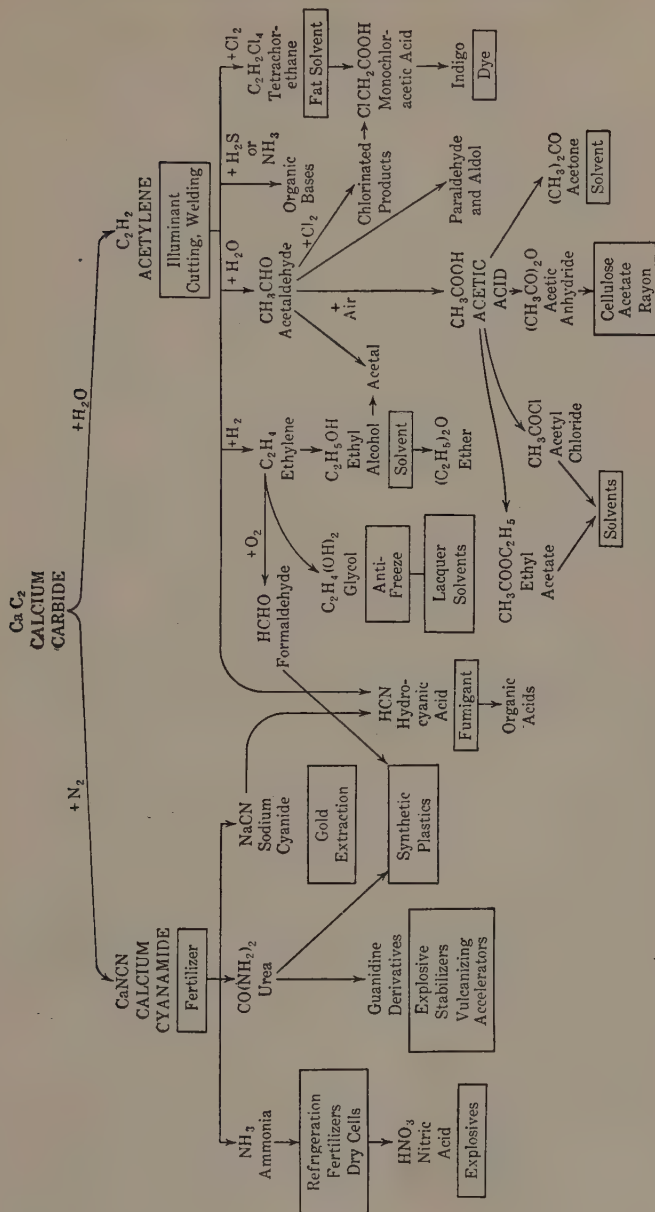
in the preparation of cellulose nitrate lacquers. By the action of chlorine and other reagents it may be converted into a number of different chlorinated hydrocarbons, which are themselves important solvents in the extraction of oils and fats from animal and vegetable products, and also the starting points in important syntheses.

Monochloroacetic acid, which is employed in very large quantities in the modern method for the preparation of indigo, may be prepared from tetrachlorethane. So even this complex dyestuff is synthesized in part from a product derived from calcium carbide. It is of historic interest that the use of chloroacetic acid in the indigo industry had most important effects in the development of chemical industry in general, for it led to the production of large electrolytic cells for generating chlorine gas, and to the development of methods for pumping chlorine gas, and induced improvements that have had much to do with the present industrial success of the so-called catalytic method for preparing sulfuric acid.

The production of all these chlorinated compounds illustrates how very remarkably the applications of chlorine in organic chemical industry have developed since the famous incident at the Tuileries, which resulted in the discovery of substitution (p. 46). The great majority of organic compounds react with chlorine, either by substitution for hydrogen, or by direct addition to unsaturated compounds, or often by oxidation. Chlorine also combines directly with other elements to form such reagents or catalytic substances as AlCl_3 , SbCl_3 , S_2Cl_2 and SOCl_2 , which are employed in great quantities in the organic chemical industries.

Not all of the syntheses we have mentioned as being possible with substances derived from calcium carbide are in commercial operation at present. The development of industry is accompanied by a never-ceasing contest, in which slight economic advantages determine the proc-

The Calcium
Carbide
Industry



esses that are in use at a particular moment. In the emergency of the World War, many synthetic processes based on calcium carbide received a development which they have not generally retained, yet many of them are still established practices. New possibilities are constantly being discovered. Acetylene and its derivatives have come to play a very important part in industries based on the great class of compounds (the aliphatic compounds) which are characterized by open chains rather than by closed rings of carbon atoms. Aromatic compounds are still for the most part derived from benzene and related hydrocarbons, obtained from coal tar.

The manufacture of calcium carbide itself is now one of the world's large industries. Its total production in the United States in 1928 was probably not far from 200,000 tons. The world's annual production of calcium cyanamide by the action of nitrogen, obtained from liquid air, on calcium carbide, is over a million tons.

Electric furnaces employed in the production of calcium carbide and calcium cyanamide have been developed from Willson's furnace of a few hundred horsepower to furnaces of 20,000 horsepower, capable of producing over a hundred tons of calcium carbide in 24 hours. The relative consumption of electrical energy has been reduced to about 60 per cent of that possible in the early days of the industry, and is now about 1.5 kw.-years per ton of nitrogen fixed in the form of calcium cyanamide. In the plants that use acetylene in chemical syntheses, the acetylene generators have sometimes been large enough to take half a ton of carbide at a charge, and a charge every hour.

CHAPTER XI

NATURAL GAS AND PETROLEUM

WE HAVE just reviewed a group of syntheses in which we began with carbon. We combined this with calcium in an electric furnace to form calcium carbide, from which a great variety of products were elaborated. Yet why go all the way back to carbon for our raw material? It would seem simpler to use products which Nature has already built up to some degree of complexity. We then need only begin where Nature leaves off, and alter or remodel the molecules of her products. That should save much of the labor that complete synthesis demands. Actually, most of the synthetic triumphs that organic chemistry boasts are based on four natural sources of organic compounds: natural gas and petroleum; coal; plants; animals. We shall devote a few pages to each.

The first petroleum well was drilled in Western Pennsylvania, in 1859. Since that day, to the end of 1929, the United States has produced over 12,000,000,000 barrels of petroleum, of 42 gallons each. This is two-thirds of the world's total in that period. The production of petroleum in the United States in 1929 was about 900,000,000 barrels, obtained from over 300,000 producing wells. This is about 70 per cent of the world's production. Petroleum pipe-lines within the United States, in 1926, extended 90,000 miles. The total investment of the American petroleum industry, in wells, refineries, pipe-lines, tank cars, storage and ship fueling stations, in 1929, was about \$12,000,000,000. Next to steel, petroleum is the world's largest

Statistics

manufacturing industry, and American railroads carry a greater tonnage of petroleum products than of any other manufactured commodity.

In association with petroleum is natural gas, which is of importance not only on account of its own industrial uses but because it supplies the pressure that lifts the petroleum to the surface in flowing petroleum wells. The United States yearly produces over 1,500,000,000,000 cubic feet of natural gas, weighing roughly 30,000,000 tons, and having a sales value of over \$300,000,000. The chief producing fields are those of Texas, Oklahoma, Louisiana, Ohio, West Virginia, Pennsylvania, California, and Wyoming. Canada and other countries produce small amounts.

Petroleum and natural gas, in spite of their present great importance, represent a vanishing resource. The United States possesses about half of the known coal resources of the world but only about one-twelfth of the world's petroleum resources. It has been estimated that at the present rate and by present methods of production the known petroleum resources of the United States will reach practical exhaustion within ten years from 1929; though improved methods that will recover much petroleum not brought to the surface by present methods may extend that time several fold. After that we shall need to depend on petroleum brought from abroad and on our oil shale reserves, which are estimated to amount to 100,000,000,000 tons. Our workable coal reserves have been estimated at 4,000,000,000,000 tons, which is sufficient to maintain our present rate of production for about 8000 years.

NATURAL GAS

The most important uses of natural gas are as domestic and industrial fuel and in the production of carbon

Uses of Natural Gas black, thousands of tons of which are used annually in the manufacture of printer's ink and as a filler for rubber (p. 208).

The natural gas is simply burned in a limited supply of air, the smoky flame depositing carbon in a very finely divided condition. The process as usually practiced is wasteful in the extreme, for the yield of carbon is only about 3 per cent. Improvements recently introduced will increase the efficiency very greatly.

A large part of the natural gas produced in the United States carries condensable gasoline vapors, which may be removed by washing it with a heavy oil, or by compression and cooling, or by absorption in finely divided ("activated") charcoal. Such natural gas gasoline, often called casinghead gasoline, supplies nearly two billion gallons yearly, which is about 10 per cent of our motor fuel requirements. It is too volatile to be used alone, but makes for easy starting when blended with other gasolines.

Natural gas consists largely of methane, CH_4 . Some millions of tons of this are available each year, yet its uses as a synthetic raw material are not yet very significant. The production of carbon black, unfortunately, is only synthesis of water and carbon dioxide, with carbon black as a trifling by-product.

Synthetic Possibilities of Methane

Recent research has disclosed catalyzers that give promise of important new syntheses based on natural gas. Catalyzers not only enable chemical reactions to proceed more rapidly than they would otherwise take place, but very often exert a selective action among several reactions, bringing one of them into prominence at the expense of the others. Very often, too, by slightly altering the temperature or pressure at which a reaction is carried forward in the presence of a given catalyzer, the nature of the products obtained may be completely altered.

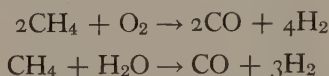
By a recent process methane may be decomposed by

heating in the presence of a catalyzer, to produce acetylene:



If this should be realizable on a commercial scale it would enable us to produce from natural gas the numerous chemical products mentioned in the preceding chapter that are derived from acetylene.

Methane also reacts with oxygen and steam at relatively low temperatures, in the presence of catalyzers, to produce carbon monoxide and hydrogen:



From the hydrogen we may then synthesize ammonia (p. 161). From carbon monoxide and hydrogen together we may produce methanol and formaldehyde (p. 219). That opens the possibility of a multitude of further syntheses, based on formaldehyde. Formaldehyde may indeed be synthesized (though not yet with profitable yields) by the direct oxidation of methane, in the presence of nitric oxides as catalyzers:



Methane may be treated directly with chlorine to form methyl chloride, chloroform, and carbon tetrachloride, as previously described (p. 109), although the best yields that have been obtained are insufficient to maintain these processes in competition with other methods for making the same products.

Natural gas contains appreciable percentages of the volatile liquids propane, C_3H_8 , and butane, C_4H_{10} . It is estimated that a million gallons of these liquids might be condensed from American natural gas each day. Ethane, C_2H_6 , a gas with practically the same density as air, is separated from natural gas by being liquefied by compres-

sion and cooling, and was used as a fuel by the Graf Zeppelin on her round-the-world flight in 1929.

The molecules of some of the heavier saturated hydrocarbons contained in natural gas may be decomposed by cracking processes, giving simpler products, such as the unsaturated hydrocarbons, ethylene, C_2H_4 , and amylene, C_5H_{10} . These unsaturated compounds combine readily with chlorine, forming chlorinated hydrocarbons, from which alcohols, aldehydes, ethers and esters of all sorts may be prepared. Or the saturated hydrocarbons may be chlorinated directly and the products converted into alcohols (p. 109).

Some of the unsaturated hydrocarbons condense to form ring compounds of the benzene or related series, when they are passed through heated tubes, or over catalyzers at high temperatures (p. 117). If there were no better way of doing it, we might even prepare perfumes and dyestuffs from natural gas.

PETROLEUM PRODUCTS

In the early days of the petroleum industry, before the automobile came to dominate the market by its demand for motor fuel, petroleum was purified and separated into marketable products by relatively simple processes. It was usually first treated with concentrated sulfuric acid, which oxidized, dissolved and removed objectionable impurities. Then the acid was drawn off and discarded, and the petroleum was washed with water and distilled in simple stills. Successive portions of the distillate were condensed in successive separate "fractions": benzine or ligroin, gasoline, kerosene, light and heavy lubricating oils, vaseline, soft and hard paraffin. In the retort there remained a black mass of petroleum coke.

Then, as years passed, petroleum fields were opened in different parts of the world that produced new types of petroleum. These needed more complicated treat-

ments. Often sulfur compounds had to be removed, and many ingenious and elaborate procedures were devised for this purpose. In the American Mid-Continent fields, and also especially in the Pacific Coast fields, petroleum was met that contained large proportions of asphaltic material—unsaturated compounds, containing oxygen. These called for special methods of refining and research directed to developing new uses for asphalt. Moreover, petroleum was often met that had to be “de-waxed”—separated from solid paraffin—before it could be conveyed in pipe lines. Various processes were developed for this, including separation by centrifuging. Finally, methods were found for decolorizing petroleum products by treating them with fuller’s earth, for removing gasoline vapor from natural gas, and for improving lubricating oils by distillation in a vacuum.

By the older methods, the proportion of gasoline obtained from the petroleum was limited by the imperfect design of the stills, and could at best approach that which the petroleum happened to contain as it issued from the ground.

Cracking Processes

The demands of the automobile soon outran gasoline production, and so compelled the development of methods that increased the yield of gasoline at the expense of the heavier and less volatile fractions of the petroleum. In brief, these were methods for decomposing the complex molecules of petroleum to form the simpler molecules of substances present in gasoline. In the earliest process this was accomplished by spraying petroleum against a wall of white hot brick. This was called “petroleum cracking.”

In 1913, Burton, an American petroleum technologist, developed a method for cracking petroleum by distilling it at high temperatures, under pressure. His process was widely adopted, but at present divides the field with many others, in some of which heat is applied to the liquid hydrocarbons to be decomposed, and in others to their

vapors. Pressures may be as great as a thousand pounds per square inch at temperatures of 900° C. A great deal of engineering research has been necessary to produce equipment that can withstand such severe conditions.

By collecting and reprocessing the heavier residues from a previous cracking process, a further yield of gasoline may be obtained, until the petroleum is almost completely converted into products that are readily volatile or permanently gaseous. Chemical engineering has given us petroleum cracking stills of three times the hourly capacity of those of 1925, without any increase in size.

An interesting recent development is the use of aluminum chloride as a catalyst in the production of gasoline by cracking high-boiling petroleum oils. Thus a catalyst which has played an important part in organic synthesis in building up complicated molecules (p. 114) is made to serve in the reverse process of decomposing complicated molecules into simpler ones. It has been estimated that as much as forty tons of aluminum chloride a day are being used in the production of gasoline. In addition it is proving useful in the refining of viscous lubricating oils. Meanwhile its applications in the synthesis of perfumes and dyestuffs are becoming more and more important.

By cracking petroleum and by recovery of gasoline from natural gas the production of gasoline has been very greatly increased. The American production of gasoline in 1928 was over 17,500,000,000 gallons, valued at \$2,-640,000,000. This was what we paid for fuel for our 23,000,000 motor vehicles! Between 30 and 40 per cent of the total gasoline production is now produced by cracking processes.

A gallon of gasoline contains enough energy to lift a weight of nearly nine tons to a height of a mile. From this it may be calculated that our yearly production of gasoline is equivalent to 94,000,000 horsepower-years of energy; in brief, to the total power of twenty Niagaras!

Gasoline
Production

Of these twenty, only one expends its energy usefully in the propulsion of the vehicles. Of the rest, about seven are engaged in heating the exhaust gases, seven in heating the radiator water, and five in radiation and general friction.

“High test” gasoline contains a relatively large amount of highly volatile hydrocarbons. This makes for easy starting in winter, but is no guarantee against “knocking,” which is caused by too rapid propagation of the explosion wave in the gasoline-air mixture. The higher the compression ratio of the engine, the worse the knocking tends to get. Each explosion delivers a sudden blow against the piston instead of exerting a prolonged push. “Straight-run” gasolines, namely those produced by distilling off and condensing the more volatile portions of petroleum, without resort to any cracking process, usually knock the worst.

To diminish knocking, straight-run gasoline is usually blended with cracked gasoline, which is relatively rich in the slower-burning, unsaturated hydrocarbons. The best “anti-knock” gasoline is produced by processes that crack the heavy hydrocarbons while they are in the state of vapor. By a careful adaptation of the cracking process to the type of petroleum used, and by skillful blending of the product with straight-run gasoline or with natural gas gasoline, knocking may often be entirely avoided. Or benzol (benzene), which is obtained by the distillation of coal tar (p. 146) may be added to suppress knocking; or perhaps a trace of lead tetra-ethyl, $\text{Pb}(\text{C}_2\text{H}_5)_4$, which is an effective “anti-knock” developed by the General Motors research laboratories.

Petroleum is available in vast quantities as a raw material from which to synthesize useful organic compounds.

Yet its applications for such purposes, as compared with coal tar, to be described in the next chapter, are comparatively slight. There are two reasons for this:

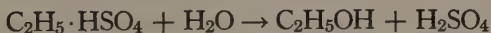
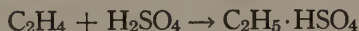
Gasoline
Quality

Petroleum
Chemicals

First, petroleum is a complex mixture of substances, ranging by insensible degrees from the difficultly condensable gas methane, through volatile liquids, to substances which can hardly be vaporized at a dull red heat, in a nearly complete vacuum. It is thus impossible to separate the components of petroleum from each other in a pure form without undue expense; and when such a chemically complex mixture is treated with chlorine or other reagents the product is still more complex. By contrast, the volatile portion of coal tar consists chiefly of only seven components, which are readily separated from one another. Petroleum, too, as raw material for synthesis, must compete with the synthetic efforts of plants and bacteria.

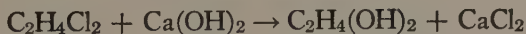
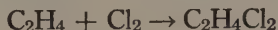
It is the weight of this competition that has prevented ethyl alcohol from being produced commercially in large amounts from ethylene, C_2H_4 , which is an important constituent of the gases produced in cracking petroleum. Ethylene combines directly with concentrated sulfuric acid, to form a compound that is readily decomposed by water, producing ethyl alcohol:

Syntheses from
Ethylene



This process has been worked commercially at various times, and now seems economically promising.

The most important products now synthesized from ethylene include glycol and its derivatives. Ethylene combines directly with chlorine to form ethylene dichloride, $C_2H_4Cl_2$, which is an important solvent. When this is decomposed by alkalis the product is glycol:



Glycol itself is an important substitute for glycerol, as

an "anti-freeze" in automobile radiators. The chief derivatives of glycol are those known by the trade names Cellosolve and Methyl Cellosolve (p. 119). These are not only important lacquer solvents but are being widely used in pastes for printing designs on textile fabrics.

A thorough study of petroleum as a raw material for the synthesis of organic compounds was made by Arthur

The Work
of Arthur D.
Little, Inc.

D. Little, Inc., about 1925. Preliminary experiments showed that when petroleum vapor is passed through long pipes, uniformly heated to about 650° C., under at-

mospheric pressure, the heavy hydrocarbons are decomposed, producing gasoline of a high anti-knock quality, together with a large yield of gas, suitable for the enrichment of water gas. As much as fifty per cent of the gas proved to consist of unsaturated hydrocarbons (ethylene, propylene, butylene, and amylene). All of these resemble ethylene in combining directly with sulfuric acid, to form compounds that are readily converted into alcohols, merely by adding water.

It was discovered that the unsaturated hydrocarbons differ enormously in the readiness with which they combine with sulfuric acid. Thus *isobutylene* is several hundred thousand times as reactive as ethylene. This fact permitted the partial separation of the unsaturated hydrocarbons by treating them with sulfuric acid of gradually increasing concentration.

Small-scale experiments were gradually extended until a plant was in operation that for a time processed 250 barrels of petroleum a day. The mixture of unsaturated hydrocarbons was made to give pure products including propyl, isobutyl, tertiary butyl and amyl alcohols. From these, various esters were prepared, especially acetates. Tertiary butyl alcohol was previously only a laboratory curiosity, but was nevertheless made and sold in tank car lots. The operations of this plant that proved most profitable are being further developed elsewhere.

CHAPTER XII

WHAT CAN BE MADE FROM COAL

COAL has been used as a fuel for more than six hundred years. In England it was first noticed along the coast, where coal veins were exposed or coal was cast ashore by the waves. This was the origin of the term "sea coal," which was long used to distinguish coal from charcoal.

The Earliest Use of Coal

Since prehistoric times charcoal had been used in the production of iron in crude furnaces, the prototypes of our modern blast furnaces. When coal began to be mined by tunneling into exposed veins it was soon discovered that it might readily be converted into coke, which would serve as a substitute for charcoal in the production of iron. Coke was first produced by setting a pile of coal on fire and covering it over with clay, with a few openings at the bottom for access of air, and a vent at the top for the escape of volatile products. Only enough air could enter to maintain a smoldering fire at the bottom of the heap, which decomposed the overlying layers of coal, expelling tar and coal gas, and leaving a solid residue of coke. This was precisely the process by which charcoal was then produced from wood.

The coke and charcoal burners of that day little suspected that the volatile products which escaped from the top of their mounds of clay would one day become the basis of a great chemical industry and were potentially much more valuable than the charcoal or coke which was left behind. The process filled the air with smoke and coal tar fumes. A proclamation of Edward I, in 1307, noted the increasing production of coke to serve as a

substitute for charcoal, "whereby an intolerable stench diffuses itself in the neighborhood, in consequence whereof the King commands the Mayor and Sheriffs of London and the Sheriffs of Middlesex and Surrey to make the proclamation that all persons wishing to exercise that mystery shall cease to use coal." London had not yet become used to a smoke-laden atmosphere.

With the invention of the steam engine and the coming of the industrial revolution coal became more important.

Coal Today Yet as late as a century ago it was just beginning to be mined in the United States, and its production elsewhere was still trifling. Wood was still the most important fuel, and charcoal was still the means for producing most of the iron and steel. The first locomotives to cross the American prairies burned wood, grown along the river courses.

The production of cheap steel (about 1860) by the Bessemer process led to the rapid extension of the railroads. Meantime the demands of the machine age for motive power grew swiftly. The forests and woodlands began to dwindle. A new fuel was needed. Coal became king. Today it dominates our whole civilization.

Coal occurs in thirty-six of the forty-eight states of the American Union. The yearly consumption of bituminous or soft coal in the United States is roughly 500,000,000 tons. Most of this is burned as fuel for domestic heat and industrial power, but at least 100,000,000 tons are heated in retorts, to supply the yearly demands of American industry for 60,000,000 tons of coke.

DESTRUCTIVE DISTILLATION

The chief products of the distillation of coal in closed retorts are coal gas, ammonia, tar and coke. Until the outbreak of the World War most of the coal destructively distilled in the United States was treated in crude "bee-hive" ovens, which had hardly been improved in five hundred

**By-Product
Coke**

years, and which permitted all the products of the distillation except the coke itself to be wasted in the atmosphere. The bee-hive is generally regarded as a symbol of industry; in industrial chemistry it is the symbol of waste.

Today perhaps 90 per cent of the by-products are saved, by processing the coal in ovens, especially designed to permit the recovery of by-products. The United States, in 1929, coked 79,000,000 tons of coal in by-product ovens, producing over 850,000,000,000 cubic feet of gas (about half of which was marketed), 890,000 tons of ammonium sulfate, 705,000,000 gallons of tar, and 210,000,000 gallons of crude benzene. The total value of these products at the place of production was over \$600,000,000.

Coal tar is a complex mixture of liquid and solid substances. Some of these are volatile, and may readily be driven off by heating the tar in a still. The
Coal Tar non-volatile residue, if permitted to cool, then solidifies into a solid pitch.

The earliest use of coal tar was probably in the production of lampblack. It was observed that tar burns with a smoky flame, which deposits soot. This was suitable for printer's ink. Then tar was gently heated to drive off the more volatile portions, and the residue of pitch was used to impregnate fabric, for roofing. This was later to become an important industry.

When the most volatile products from coal tar were condensed a light liquid was obtained, which was found to be useful as a fuel for lamps, and as a solvent. A century ago, rubber-coated fabrics were just becoming known in the markets of the world. The light liquid from coal tar was found to be an excellent solvent for rubber, and has been used in great quantities for that purpose in the manufacture of rubber goods, since the discovery of vulcanization by Goodyear, in 1839 (p. 205).

Meanwhile, less volatile products, distilled from coal

tar, came on the market as an oily, evil-smelling liquid known as coal tar creosote. Wood impregnated with this was found to resist decay. This was in the days of the first steam railroads (1838). Then the telegraph was invented. Railroad ties and telegraph poles were impregnated with coal tar creosote, as a protection against decay, at first in an experimental way, and later on a larger scale, the world over. Billions of board feet of

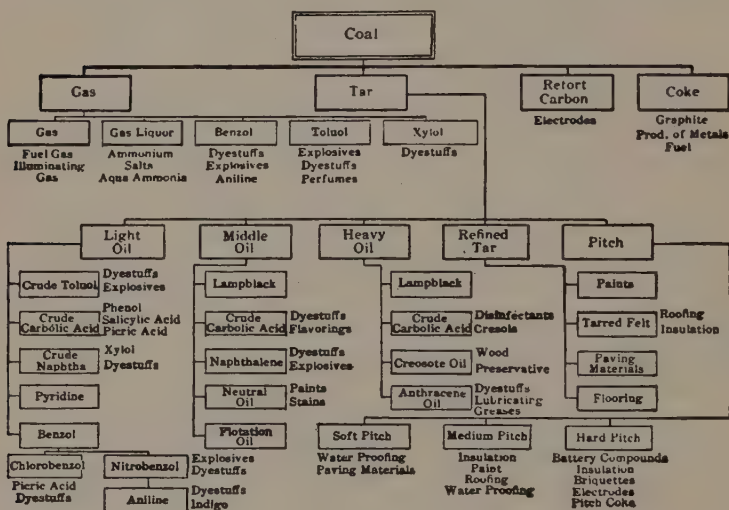


FIG. 13.—COAL TAR PRODUCTS

wood have been treated, and creosote is still the most important wood preservative.

So, by the time coal came to be extensively used as a fuel, the destructive distillation of coal in retorts was a well-established industry, coal gas was being burned in most large cities, and coal tar had been made to yield lampblack, roofing, illuminants, solvents and wood preservatives. Since that time coal tar has become an important road-making material, has been extensively used in rubber compounding (p. 208), and in the production of substitutes for hard rubber (p. 199). Atomized with

steam or compressed air it is readily burned under boilers. Millions of gallons are so used every year, in spite of all other demands. Yet more interesting and significant uses still were about to be discovered for coal tar. The organic compounds present in this unattractive black fluid have most amazing synthetic possibilities.

DYESTUFFS

In 1845 A. W. Hofmann, a pupil of Liebig, found that the light oil distilled from coal tar contains benzene. Faraday had already noted the presence of this substance in gas-oil (p. 37). Benzene may readily be converted into aniline, $C_6H_5NH_2$, from which the British chemist William Henry Perkin, at the age of seventeen, produced the first coal tar dye (1856). In an attempt to produce quinine, Perkin oxidized aniline with chromic acid. The result was a violet dye, which he christened "mauve." So vigorously did he follow up this discovery that within a year he had a small factory in operation, producing mauve for the market.

Yet no industry can hope to prosper that seeks to exploit a chemical product produced in such an offhand way, with no knowledge of its structural formula, nor any very thorough study of its properties. Mauve was not really a very satisfactory dye, for it lacked, among other qualities, resistance to light. Almost immediately, too, it had to meet the competition of other dyes, made by oxidizing aniline and related substances with various oxidizing agents. Yet Perkin's discovery did awaken interest in the problem of producing dyes by artificial means, and so laid the foundations of the synthetic dyestuff industry of today.

Twelve years after Perkin's discovery of mauve, two German chemists, Graebe and Liebermann, synthesized alizarin, or "Turkey red"—an important dyestuff formerly obtained only from roots

The First
Coal Tar Dye

Alizarin

of the madder plant. The next year Perkin himself discovered a better method for preparing it, employing reactions which the earlier pages of this chapter have de-

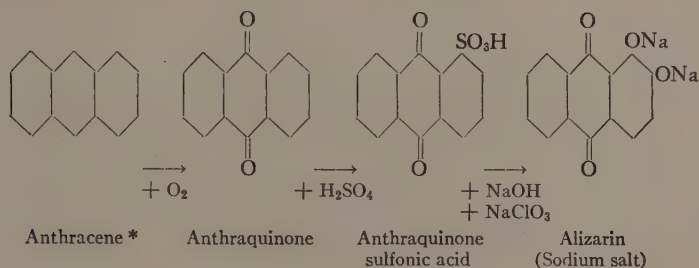


Courtesy of Parke-Davis and Co.

THE FIRST COAL TAR DYE

scribed. The solid hydrocarbon, anthracene, which is one of the less volatile products obtained in distilling coal tar, is gently oxidized. The result is anthraquinone. This is sulfonated (p. 110), producing anthraquinone-sulfonic acid; and this in turn is heated with caustic soda,

under conditions that favor oxidation. The result is alizarin:



Alizarin is a beautiful red dye, used especially for wool. We may note two hydroxyl groups in neighboring positions on one of the rings. The discovery of this means for synthesizing alizarin itself led to research that soon produced other dyes, having two hydroxyl groups in other than neighboring positions, or having three, four or five hydroxyl groups spaced round the two benzene rings. These dyes are of different colors, and by use of different sorts of mordants may be made to give other shades still. A mordant is something that is used to enable the dyestuff to adhere more tenaciously to the fiber; commonly it combines chemically with the dyestuff or fiber, or both.

Mauve had been something new. But alizarin was a natural dyestuff known and used for centuries, and was the first of the natural dyestuffs to be duplicated in the chemist's laboratory. Its synthesis was an immediate commercial success, and within ten years the great madder-growing industry in France was virtually extinct. In regions formerly devoted to the cultivation of that plant, peasants have been heard to remark, "No one grows madder any more, since it is now made by machinery."

If alizarin could be made in the laboratory, why not other natural dyes? The queen of these was indigo, a beautiful blue, produced by the indigo plant of the tropical Orient. For at least thirty-five centuries it had held a leading place in the

Indigo

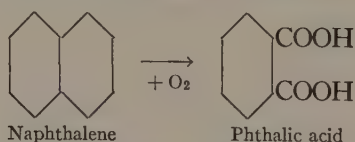
* We have here used abbreviated formulas, as explained on p. 69.

dyer's art, and vast areas in India, Java and China were devoted to its culture.

Chemists set to work at once, but soon discovered that this was a problem not to be solved so easily. A German chemist, Baeyer, did succeed in producing indigo, within one year of the synthesis of alizarin, but by a method which was not commercially practicable, and which threw little light on the structural formula of the substance. Indigo happens to be a much more complex substance than alizarin, and when decomposed in various ways, it gives the most varied products.

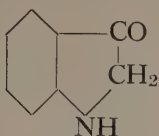
Ten years were spent in an endeavor to guess from a study of these fragments of the indigo molecule what the structural formula of indigo itself might be. At last, in 1879, that question seemed settled. Baeyer then devoted further years to new syntheses of indigo, based on its structural formula. Yet these still proved commercially impracticable, for they made use of expensive raw materials. Another German chemist finally discovered a synthesis from a cheap material, naphthalene (obtained from coal tar). Yet many more years were needed to overcome the obstacles that stood in the way of the production on a large scale.

As the process at length was developed, naphthalene was oxidized, forming phthalic acid.* The method now generally used is an American invention:

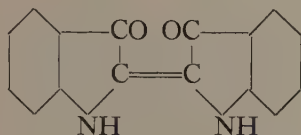


Then, by numerous separate steps a second ring, containing nitrogen, was built on to the benzene ring of the phthalic acid, thus producing *indoxyl*:

* We have already noted that when a chain of carbon atoms attached to a ring is oxidized, the chain is changed to a carboxyl group, —COOH. Here, the second benzene ring is oxidized, giving rise to two carboxyl groups.



When this was agitated with air, two molecules combined, forming *indigo*:



On paper the synthesis looks easy enough. Yet the effort took forty years of time (1869–1909), cost millions of dollars, and was successful only when to the research of a generation of synthetic chemists had been joined a new type of research—that of the chemical engineer.

The United States now produces over 10,000 tons of synthetic indigo a year, and an even greater amount is manufactured in Europe. The great indigo plantations of the Orient have almost disappeared. Yet when two great industries compete for the world's markets, science lends its aid to both contestants impartially. Scientific methods, applied to the cultivation and harvesting of the indigo plant and to the discovery of better methods of extracting and purifying indigo from the leaves and twigs, give promise of maintaining a remnant of this ancient industry in the face of the competition of artificial indigo. The synthetic chemists and chemical engineers, at the end of their forty years of effort, have had to rest content with less than a complete victory.

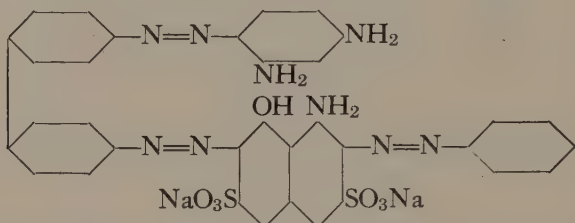
During the years that it took to establish the synthetic indigo industry, hundreds of other dyestuffs were produced from compounds present in coal tar.

Other Coal Tar Dyes

Dyestuff manufacture starts from the coal tar hydrocarbons, such as benzene, toluene, naphthalene and anthracene, or from phenol or cresol,

and produces derived substances called intermediates, such as nitrobenzene, aniline, phthalic acid, nitrophenols, nitranilines, and others. These, by complex reactions, are elaborated into dyes.

Many of the modern dyestuffs are of extremely complex constitution. A fair sample, no more complicated than hundreds of others, is Pontamine Black EX, which is used for dyeing hosiery, and has the formula:



A molecule of this dye contains seventy-nine atoms, each in its proper place with respect to all the rest. In that respect a dyestuff molecule is a pretty elaborate unit. Yet the dyestuff industry has so mastered the art of quantity production that four hundred thousand million million of these units—making altogether one pound—can be sold for a dollar.

Many of the synthetic dyestuffs produced in the earlier years of the industry were fugitive toward light or were unsatisfactory for other reasons. Yet as years passed a much greater range of colors was produced by synthesis than plant dyes had been able to offer. The best synthetic dyes are more brilliant than the natural dyes of similar hues and are much more resistant toward light or laundering. Logwood, a black dye extracted from a Central American tree, is still of importance in the coloring of wool, silk and leather. Fustic, a yellow dye for wool, is extracted from another wood. The rest of the natural dyes have been almost completely driven from the market.

In 1906, fifty years after the date when Perkin, as a lad of seventeen, discovered the first coal tar dye, the

synthetic dyestuff industry celebrated its golden jubilee with a banquet in New York City. Sir William Henry Perkin himself was there as the guest of honor. Thousands of tons of dyestuffs of hundreds of different sorts were then being produced each year from coal tar, chiefly in Germany. The dyestuff industry had moved across the North Sea, from the land of Faraday, Frankland and Perkin to the land of Liebig, Wöhler, Kekulé and Baeyer.

In recent years many new classes of dyes have been created, and important additions have been made to classes formerly known. Several thousand synthetic dyes, derived from coal tar, are in actual use. Rayon and cellulose acetate fabrics, particularly the latter, have in part called for new methods of dyeing and new types of dyes. Rapid progress has also been made in the art of applying dyes to fabrics, especially since 1920. Old processes have been simplified and new ones have been worked out that take advantage of suggestions offered by the structural formulas of the synthetic dyes themselves. The natural dyes, by contrast, being often of unknown chemical structure, had to be applied to fabrics by rule-of-thumb methods that grew out of methods of the dyer's art inherited from ancient times.

One of the recent achievements in dyeing practice has been the discovery of methods for "immunizing" cotton, that is, so treating it that it fails to be dyed by ordinary cotton dyes, but is dyed by the highly basic dyes developed for cellulose acetate. By weaving threads of immunized cotton into cotton goods, then dyeing, washing, and redyeing with a basic dye, many beautiful color contrasts can be obtained.

Since the World War the dyestuff industry has been much more widely distributed than before. The nearly complete monopoly which Germany formerly held has been terminated (see table, p. 234). The United States, in 1928, produced 44,000 tons of synthetic dyes, which

Recent
Progress

was about 94 per cent of its own requirements. The important industrial countries of the world have all made a special effort to become self-contained with respect to dyes, since the dyestuff industry is a great training field for organic chemists, who may be transferred to other tasks in time of national need. The dyestuff factories themselves may be diverted almost overnight from the manufacture of dyes to the production of poison gas for gas shells. Phosgene, COCl_2 , for example, is not only used in the production of an important class of dyes but is itself a war gas. In general dyestuff factories and munitions factories use the same raw materials and employ the same chemical methods.

SYNTHETIC PERFUMES

It was early noted that many of the raw materials and intermediates of the dyestuff industry might readily be converted into compounds of pleasant odor. Benzaldehyde, for instance, has an odor suggestive of almond blossoms; phenylethanol, a rose-like odor; and vanillin, a part of the odor and flavor of vanilla. Artificial violet perfume and artificial musk, derived from coal tar compounds, are marketed at less than 1 per cent of the price formerly commanded by the natural products. Other synthetic products have been incorporated in blends that exactly imitate the perfumes of the heliotrope, lilac, geranium, orange-blossom, lily-of-the-valley, tuberose, jasmine, hawthorn and carnation.

The synthesis of perfume compounds is rather simpler than the synthesis of an average dye. Yet when the pure compounds have been prepared, their
Blending blending, to duplicate a particular natural product, requires a great deal of further experimentation. Traces of a substance of powerful odor may completely alter the odor of something else that is present in predominating amount. In the synthetic blends of today

many organic compounds are used which have long been known but which have only recently been known in sufficiently pure form, or have only recently been appreciated as ingredients of perfumes.

Since perfumes have been very much decreased in price by the development of synthetic products, they are being used in much greater quantities than ever before, as ingredients of mixtures that formerly were odorless or of unpleasant odor. A trace of a properly selected perfume may exactly offset the slight rancid odor that is sometimes developed in finishing woolen goods.

EXPLOSIVES

Many of the dyestuff intermediates are nitro compounds. Other compounds of the same class are useful as explosives. One of them, picric acid or trinitrophenol, was even used as a dye for many years before its explosive character was discovered. Other important explosives of this class are trinitrotoluene (TNT), hexanitro-diphenylamine, and the nitronaphthalenes. Their explosive action depends on the fact that they contain enough oxygen, loosely connected with nitrogen in the nitro groups, to oxidize a large part of the carbon in the compound to carbon monoxide.

The explosives of this group need to be set off by the shock of a detonator, that is, a more sensitive explosive compound, such as mercury fulminate, or
Detonators tetranitro-methyl-aniline (tetryl). This, as it were, jars the oxygen atoms loose from the nitrogen atoms, leaving them free to combine with the carbon, which they do without delay. The result is a sudden and violent evolution of gas, the disruptive effect of which is increased by the heat that is liberated.

The explosives we have named all detonate with especial violence on being set off with a fulminating cap. This makes them useful when a shattering or rending effect

needs to be produced, as with high explosive shells. Yet in spite of this they are much less unstable chemically than the more slowly burning propellant explosives, such as smokeless powder (p. 182). Picric acid and TNT are regularly melted and poured, in filling shells. Another high explosive is a mixture of 80 per cent ammonium nitrate and 20 per cent TNT, which is heated until the TNT melts, forming a plastic mass, much like a mixture of sugar and butter. This is rammed into steel canisters.

MEDICINALS

At the very moment when Perkin discovered mauve, attempts were being made in England to render sewage less obnoxious and less of a menace to public health by treating it with crude carbolic acid (phenol). The success of these experiments led the British surgeon Lister (1860) to conclude that phenol must be an effective germicide. The result was antiseptic surgery, in which the physician's hands and instruments were sterilized with a solution of phenol. For years, indeed, Lister and his assistants worked with their hands in a fine mist or spray of phenol solution, until it was shown that it was really unnecessary thus to attempt to destroy any bacteria that might be floating in the air of the operating room. If harmful bacteria had really been present in the air the spray would have been ineffective.

This was the beginning of the use of coal tar compounds in medicine and surgery. Phenol is still a useful germicide, though it is by no means so important for that purpose as it is in the manufacture of dyestuffs, explosives, synthetic resins (p. 191) and medicinals. It is used in the synthesis of salicylic acid and methyl salicylate (oil of wintergreen); such well-known medicinals as acetyl salicylate ("aspirin"), phenacetin and salophen; and some important arsenical compounds used in combating sleeping sickness, relapsing fever, and syphilis.

During the World War some remarkable antiseptics known as the chloramines were developed. These are derived from toluene. From toluene, too, are synthesized benzoic acid and numerous derivatives of benzoic acid, such as benzaldehyde (oil of bitter almonds), benzyl benzoate, a non-habit-forming synthetic substitute for morphine, and saccharin (the "super-sweet").

To Robert Koch, one of the founders of the science of bacteriology (p. 249) we owe the observation, about 1880, that bacteria may often be stained with coal tar dyes, on a microscopic slide, to make the bacteria show in contrast with other material. This discovery has been of great assistance in the microscopical study of disease-producing micro-organisms. Koch even hoped to combat the tuberculosis bacillus within living human patients by finding some dye which would kill the bacillus without affecting human tissue. He was disappointed in this hope, but other micro-organisms have been controlled by the administration of dyes.

Trypan red and trypan blue have been used in sleeping sickness; methylene blue in nephritis and rheumatism; and scarlet red in stimulating the growth of new tissue in wounds. Two recently discovered yellow dyes, proflavine and acriflavine—both produced from aniline—have proved to be several hundred times as effective germicides as our standard germicide, phenol; yet they are non-toxic and non-irritating when used to disinfect wounds. Even the famous arsenical, salvarsan, is a yellow powder, which might be used as a dye.

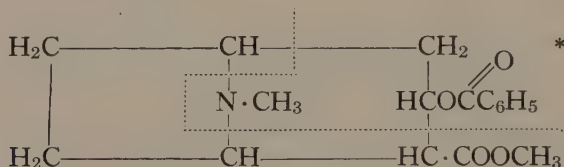
The dyes that have been used in combating the diseases we have named in general contain groups of atoms that enable them to penetrate the micro-organisms, and other groups that render them more toxic to the micro-organisms than they otherwise would be. The result is much as if our microscopic enemies were to be hunted down individually and shot full of poisoned arrows.

Dyestuffs as
Medicinals

For decades the most important local anesthetic was cocaine, which is a nitrogenous compound belonging to the group of alkaloids (p. 298). Yet cocaine is a toxic substance, and severe symptoms of poisoning frequently followed its use in deadening pain. The obvious remedy was to determine its structural formula, then alter that structure in such a way as to get rid of toxicity without losing the capacity for deadening pain.

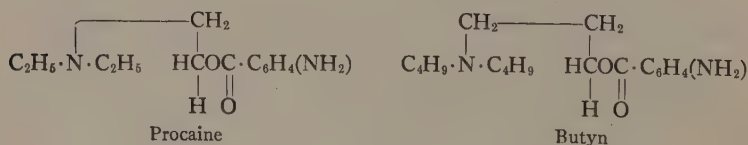
**Local
Anesthetics**

Some years of research at last disclosed the structural formula of cocaine:



As soon as this information had been gained, organic and physiological chemists set to work to synthesize and test new compounds, having molecules built upon architectural plans resembling that of cocaine, but with modifications. Thus it was presently discovered that only the portion of the cocaine molecule that is marked with a star—above and to the right of the dotted line in the preceding formula—is responsible for the capacity of cocaine for deadening pain. The rest of the molecule is worse than useless, for it contains groups that relate the substance to nicotine and poison hemlock.

The result is that cocaine has been very largely displaced by synthetic alkaloids, derived from coal tar compounds, and quite unknown in nature. Examples are:



A glance will show that these substances contain the groups specified above as necessary to a local anesthetic of this type, and very little else. These products, and a number of other closely related synthetic alkaloids, are safer than cocaine, because less poisonous. Furthermore, they are more stable toward heat, and therefore more easily sterilized.

The story of synthetic local anesthetics shows very plainly that medico-chemical research is no longer limited to attempts to purify or even to attempts to synthesize compounds of medicinal value that happen to be produced by plants and animals. It seeks rather to use these compounds as starting points or sources of suggestion for researches that explore the physiological effects of particular groupings or configurations of atoms within the molecules of synthetic compounds.

NEW METHODS FOR PROCESSING COAL

What has preceded relates chiefly to the products that may be made from compounds present in coal tar. The tar itself is obtained by heating coal, out of contact with air, now chiefly in by-product ovens. Yet the by-product oven is a triumph of engineering, not of chemistry. Until quite recently no very effective research has been done on the fundamental problem of the conditions of temperature, pressure, fineness, and rate of heating under which coal should be distilled in order to give products of greatest industrial value.

All this is being changed. A great many methods have been proposed whereby soft coal and lignite (sometimes called brown coal) are coked at relatively low temperatures (below about 750°C.). The result is a solid semi-coke, coal gas, and tar.

The semi-coke itself burns with a smokeless flame, and is particularly suited for use as a domestic fuel. It has

been estimated that the annual smoke damage in New York City alone, due to costs of cleaning buildings, extra costs of laundering and the wear and tear of too frequently laundered fabrics, amounts to \$170,000,000.

The gas produced in the low temperature coking process has a higher fuel value than ordinary coke-oven gas, but there is less of it. Very little ammonia is produced. The remaining product is low-temperature tar, about 25 gallons for each ton of soft coal. This presents the great problem which must be solved if low temperature coking is to be a commercial success. The compounds that low-temperature tar contains are very different from those present in ordinary tar, and to a large extent belong to aliphatic rather than aromatic classes of compounds (p. 68). Much investigation will be necessary before their industrial possibilities can be fully developed.

In Europe, at least, the most promising present use for low-temperature tar is in the production of motor fuel. The German inventor Bergius has developed a process in which tar, or even soft coal or lignite, is treated with hydrogen at about 650° C. under pressures as high as 3000 pounds per square inch, sometimes in the presence of a catalyzer. The tar or coal is thereby in part converted into liquid hydrocarbons analogous to those of petroleum.

For the moment, low-boiling products, corresponding to gasoline, are chiefly desired, though lubricating oils will doubtless soon be produced. The yield is from 90 to 140 gallons of liquid hydrocarbons from each ton of coal. Gasoline derived from this liquid is of excellent anti-knock quality and is already of great importance in Germany, as it probably soon will be in other countries that are without important petroleum resources of their own. (See p. 230.)

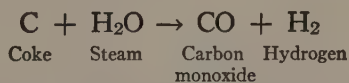
The reader will have noticed that one of the trends of the recent developments which we have sketched in

**Motor Fuel
From Coal**

this and previous chapters is the increased importance of reactions that are carried out in the presence of catalyzers under high pressures. The production of ammonia by the direct union of nitrogen and hydrogen under pressure is the outstanding example in the inorganic field. These processes owe their development to chemical engineering skill, for it was necessary to develop new materials and new methods of handling old materials when hydrogen needed to be used under pressure at high temperatures, or when corrosive gases, such as chlorine, nitric oxide fumes or hydrogen chloride had to be applied at high temperatures. Industrial chemistry would not have reached its present development without the support of the engineer, and of financial interests with the faith and courage to pour money into the investigations over a period of many years.

SYNTHESIS FROM COAL GAS

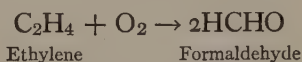
With all this the story of the industrial possibilities of coal is far from complete. We have said nothing of coal gas and coke as synthetic raw materials. Coal gas is about one-third methane. This may be converted into acetylene and its derivatives, as already mentioned (p. 136). And about half the million million cubic feet of coal gas produced each year in the United States is hydrogen. This amounts in all to more than a million tons of hydrogen. To that we may add the hydrogen contained in water gas, which is produced by the action of steam on coke:



Thus an unlimited supply of hydrogen is available for the production of ammonia by direct synthesis, together with a supply of carbon monoxide for the synthesis of methanol (p. 219).

Coal gas usually contains several per cent of ethylene. This offers the possibility of the production of ethyl alcohol and glycol, by methods previously described (p. 142). The percentage of ethylene in coal gas is nevertheless much smaller than in the gas produced by cracking petroleum vapor, hence the latter has a great economic advantage as a raw material for such syntheses.

It is interesting to note that ethylene may readily be oxidized to formaldehyde, with a 70 to 90 per cent yield, in the presence of a catalyzer of boric acid or phosphoric acid:



This promises to be of commercial importance.

The applications of coal and coal tar that have been related in this chapter have all been accomplished without any very thorough knowledge of the chemical differences between different types of coal. It is only by good luck or the beneficence of Providence that in subjecting an imperfectly studied raw material to haphazard methods of distillation we have obtained so many products that industry can use. In the future we shall be able to proceed in developing still further uses for coal in the light of a better understanding of its own chemical nature. Bergius has recently obtained a product having the chemical composition and all the general characteristics of coal, by heating cellulose with water at 340° C. under high pressures.

Other lines of research seek to revolutionize the iron and steel industry by the use of coal gas or water gas in the reduction of iron ore. New methods are constantly developed for lowering the ash content of coal or for producing smokeless briquets from slack coal or anthracite culm. A successful explosion motor has been developed, fuelled with coal dust instead of gasoline or oil.

Looking
Forward

The particular developments that each part of the world will carry furthest will be those that serve it best. In one country, lack of petroleum resources may lead to the production of liquid fuels on a large scale by the hydrogenation of coal or tar. In another, it may be more economical to convert the coal as completely as possible into gas, in the vicinity of the coal mine itself. Gas will there be used industrially to the fullest possible extent, will be transported long distances in high pressure mains, and will be extensively used as raw material in chemical synthesis. In either event, coal as a fuel, in its natural state, unmodified by the chemist, will constantly become of less importance.

CHAPTER XIII

THE CELLULOSE INDUSTRIES

THE most abundant product of plant life is cellulose, $(C_6H_{10}O_5)_n$.^{*} Intermingled or combined with other material, it makes up most of the woody or fibrous parts of plants. It forms the framework of the plant, the skeleton, as it were, which is clothed with the tissues that are engaged in more vital work than that of merely giving form and support. If all the plant material of the earth were gathered together into one great heap, nearly half of the total dry weight would be cellulose.

As lumber and shingles or palm thatch or straw, cellulose furnishes shelter for most of the human race. As linen, cotton or ramie, it forms our most important textiles. As paper, it serves as a medium of communication between men and nations and aids civilization by recording the advances won by each generation for the benefit of generations to come. The coal measures of the earth, which furnish us with heat and motive power and the raw material for a multitude of chemical industries, have been chiefly derived from cellulose furnished by plants that grew upon the earth in former geological ages.

The great industries that are based on cellulose nearly all use that material almost as it is furnished us by Nature. Wood may at most be given a protective coating or may receive a chemical treatment to render it more resistant to fire, insects, or decay. Linen and cotton may be puri-

^{*} The subscript n indicates that the cellulose molecule is an undetermined or indefinite multiple of the group $C_6H_{10}O_5$. But see p. 292.

fied by being boiled with dilute alkali, and may be bleached and dyed before being woven into fabrics. Yet the product is cellulose, practically unaltered. Paper is produced by felting natural cellulose fibers into a continuous sheet.

Even rayon is still cellulose. The chemist merely gives the natural material a more attractive physical form, by spinning it into fine threads. The chief contributions of chemistry in the cellulose industries have not been in synthesis, but merely in purifying the cellulose raw material, or in separating it from other materials with which it is associated in plants. This has been accomplished in almost complete ignorance of the chemical nature of these materials. The structural formula of cellulose itself is still incompletely determined and the only useful products of industrial importance that are derived from it by chemical synthesis are the nitrate and acetate esters.

It was in China that the art was first developed of causing plant fibers to felt or mat together into continuous sheets, which could be given a smooth surface, suitable for writing. The result was paper, which became known to the Arabians about the Eighth Century, and was carried by them to other Western lands. It did not come into common use in Europe until the Thirteenth Century.

The first paper was made from cotton and linen rags, which are still used for some of the finer grades. Later other sorts of plant fibers were introduced, particularly those obtained from wood. Whatever the nature of the raw material, it first receives a preliminary treatment to remove dirt, or other objectionable material. Following the preliminary treatment the stock is treated with hot solutions of chemical reagents to remove the non-cellulosic impurities as completely as possible. The pulp so made is then washed to remove traces of the chemicals used in digesting. This operation is followed by bleaching and another washing. The pulp so prepared is used,

either alone or in conjunction with other pulps, and frequently in conjunction with fillers and size, in making paper.

Following the pulping operation, the pulp is suspended in water in a beater. In this the fibers are drawn out, the ends are frayed and split off into slender fibrillae, and customarily the fibers themselves are cut into shorter lengths.

Paper-making
in Outline

In addition, the beating process causes the fibers to become hydrated, that is, to combine chemically with a variable amount of water. If this process is carried far enough the material becomes gelatinous and gives a relatively translucent sheet as a final product. The various operations carried on in the beater aid the material to felt or mat together in the subsequent paper-making process. The beater is also used for the addition of fillers, such as clay in the manufacture of book paper, or size and alum, which render the paper resistant to penetration by ink.

Until about a century ago paper was made by hand, the wet web being removed from small screens, pressed, dried, and finished. Some expensive grades of paper are still made in this way, but paper would never have become cheap and plentiful had not Robert, in France (1798) and Fourdrinier, in England (1803) developed a machine in which pulp suspended in water flows continuously onto an endless, fine-mesh, wire screen. This moves forward continuously over table rolls, at the same time being shaken sidewise to induce the fibers to mat together and cross-grain.

While passing over the wire most of the water is removed. This process is aided by suction boxes. The continuous, wet sheet or web thus formed is transferred from the wire to a felt, which carries it between one or more sets of press rolls, to remove more water. Commonly the direction of travel is reversed once, so that both sides of the sheet will come in contact with a smooth roll. Next

the web is carried over hollow, cylindrical, steam-heated driers, where the remaining water is removed. The paper then passes through a so-called calender stack, which consists of rolls that press and smooth the finished web. Frequently it is given further finishing operations.



Courtesy of Banning and Seybold, Düren

PRESS PART OF A HIGH SPEED FINE PAPER MACHINE

Wood is now the most important paper-making material. Much of it receives no chemical treatment whatever.

Mechanical Wood Pulp Logs of spruce or hemlock are carefully freed from bark, then pressed against revolving grindstones, while being wet with water. The wood fibers, thus torn away, are screened to separate coarse material. The pulp is then mixed with chemically treated fibers, and passes directly to the paper-making system.

Over 500,000 tons of such ground wood, sometimes called mechanical wood pulp, are produced in the United States each year. This represents about 500,000 cords of wood. Ground wood makes up about 80 per cent

of ordinary newsprint stock, the rest usually being chemical wood pulp, usually produced by the sulfite process, presently to be described. Mechanical wood pulp is by far the cheapest of all paper-making materials, but is subject to destruction by slow oxidation. Newspapers within a few years turn yellow and fall to pieces. No records that are designed to be permanent are ever committed to paper that is known to contain ground wood. Unfortunately, the short life of this material was not recognized for many years after its introduction into the paper-making industry about 1860, and much of the literature of the decades that followed will need to be re-printed on paper of a better quality if it is not to be lost.

About 1880 an American chemist discovered that when wood chips are heated in a closed vessel with a liquid produced by saturating slaked lime with sulfur dioxide gas, the non-cellulosic material is very largely dissolved and removed, leaving a purified fibrous pulp suitable for paper-making. The process was further developed in Europe, then brought back to the United States, where it became the basis of a great industry. Serious engineering difficulties that were found in the beginning have been completely overcome. At the present time over five million cords of spruce, balsam and hemlock are now converted into paper pulp by the sulfite process in the United States and Canada each year. In addition, we import large quantities of sulfite pulp from Scandinavia. The world's annual production of wood pulp, by all processes, is above 7,000,000 tons.

The sulfite pulp industry is not one of which the chemist may be very proud, for it was developed with very little understanding of the chemical nature of the substances that need to be dissolved and removed from wood, in order to set the fibers free. These substances make up about half the organic matter in the wood and

The Sulfite Process

amount to many millions of tons every year. Nevertheless sulfite liquors are generally run to waste, polluting streams, killing fish and creating a general nuisance.

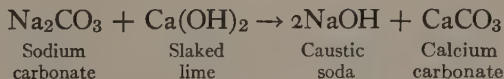
Numerous attempts to put this waste material to use have of course been made. It has found some employment as a binder in fuel briquets. Someone has recently found that sulfite liquor may be mixed with formaldehyde for the production of a heat-hardened resin analogous to those made from phenol and formaldehyde (p. 192). If this proves to be a practical invention, the present widespread use of synthetic resins, described in the next chapter, will be even further extended.

Poplar and similar woods are often treated by the soda process, in which wood chips are digested under pressure with a dilute solution of caustic soda.

Soda and
Sulfate
Processes

This process is better suited than the sulfite process for the treatment of the broad-leaved species of woods. Pulp made by it has neither a long nor a strong fiber, yet may be used in conjunction with sulfite and rag fibers, and contributes a good surface for printing, as in book papers. In England, paper is made by the soda process from esparto, a perennial reed imported from Spain and Northern Africa.

The spent caustic soda solution discharged from the digesters is evaporated to dryness. The solid residue is then heated in a furnace until the organic matter burns away, leaving crude sodium carbonate. This is dissolved and reconverted into caustic soda by treatment with slaked lime:



Because of the drastic action of the caustic soda on the fiber, a modified method has been developed, which employs a solution containing sodium sulfide, together with a small amount of caustic soda. This method was first used in Dantzig in 1883, and introduced into the United States

in 1907. In 1929 about 1,000,000 tons of paper pulp were produced by this process, in the United States alone.

The process just described is called the Kraft or sulfate process. The latter name refers to the use of sodium sulfate to regenerate the sodium sulfide which is the actual reagent. One of the advantages of this process is that it operates successfully with resinous woods, such as Southern pine, which cannot be cooked by the sulfite process. Tough, strong wrapping paper is now generally made by this process.

This by no means completes the list of reagents used in paper-making. Among others that have been suggested, chlorine seems very promising. It produces a very pure, white pulp. It has recently been shown that the sulfurous acid of the sulfite liquor, rather than the lime, is the active reagent in the sulfite process. A process has been developed which uses sulfurous acid alone, and which is particularly successful with cereal straws. Each fibrous raw material brought forward for paper-making and each separate kind of paper on the market calls for special treatment, and constant progress is being made in the development of new methods.

The total annual production of paper and paper board in the United States by all processes is over 8,000,000 tons. Paper has many important uses other than its use for recording the written or printed word. Square miles of wrapping paper, roofing paper, builder's tarred paper and wall paper are produced every year. Truck gardeners are using weatherproofed paper to keep down weeds and reduce evaporation in fields of garden crops. Transparent oil-proof "glassine" paper is used for wrapping or packaging greasy foods. A very thin, non-porous paper of high dielectric strength is used in great quantities in condensers, in the radio industry. Paperboard, impregnated with synthetic resins, forms insulating panels for

Other
Processes

Special Uses
for Paper

electrical switchboards and panels. The production of paper towels and napkins, wallboard and corrugated paperboard are important industries. Even car wheels have been made of paper, forced by hydraulic pressure into steel rims.

Kraft paper, twisted into yarn, is used as a substitute for rattan in making furniture. Rugs, hats, and even articles of clothing woven of paper yarn have been rather widely used. Nevertheless a product prepared by felting short fibers, as in paper-making, can never be very strong.

Our resources of wood available for paper-making have been dwindling so rapidly that the time has seemed not far distant when other materials would have to be substituted for wood in paper-making. Thousands of different plants have been tested, and dozens have proved promising if we consider merely the quality of the paper produced. Yet esparto alone has proved successful in competition with wood, and even this is practically limited to England. The costs of fortune in paper-making are strewn with the wreckage of ambitious enterprises which have sought to exploit flax, reeds, grasses, bamboo, sugar cane bagasse and cornstalks. The paper they produced was often excellent, but wood possessed economic advantages that they could not overcome.

After all, the paper industry uses only about 4 per cent of the wood cut from our forests. Wood is being replaced in many of its uses by metal, concrete and moldable synthetic plastics (p. 183), presently described. Moreover, several great paper companies are engaged in extensive reforestation projects, designed to furnish a perpetual supply of pulpwood. The threat to our forest reserves is much less serious than it was a few years ago. At worst, the reserves in certain parts of the United States and Canada may be exhausted, driving the paper pulp industry elsewhere. Great forests of pine and hardwood suitable for paper-making still exist in the South. Within

Wood
Substitutes

the United States, at least, another material may hope to replace wood only if it can be delivered almost cost-free at the pulp factory, as a by-product of some other agricultural industry.

In the world at large the most economically promising substitute for wood available in great quantities is at present bamboo. Its introduction into the markets of the world as a material for paper-making seems to await only cheaper methods of harvesting and a more thorough study of the behavior of bamboo of different species when subjected to different chemical processes.

Cereal straws have been widely used in the manufacture of paper board and coarse wrapping paper. By the sulfur dioxide process or by the chlorine process, even the better grades of paper can be produced from straw, and there are perhaps localities in which straw can be made to compete with wood. Flax straw, which is available as a waste material by millions of tons in Minnesota and neighboring states and provinces, has some promise.

Bagasse (the waste fibrous residue obtained in extracting sugar from the sugar cane) is worked into insulating board and wall board on a large scale. Recently, indeed, fibrous varieties of cane of low sugar content have been grown especially for the insulating board industry. Any attempt to use bagasse for better varieties of paper will need to compete with this industry as well as with wood. Otherwise, bagasse, when freed from the pithy material, makes first-rate paper.

Repeated unsuccessful attempts have been made to use cornstalks in paper-making. About 200,000,000 tons
Cornstalks are available in the United States each year. The difficulty is that there is hardly 30 per cent of useful fiber in the stalks. The rest is largely pith. If this is eliminated the yield is too low for cornstalks to compete with wood. If the pith is left in, the result is a harsh, rattly, translucent sheet, which is

readily torn. Cornstalk enthusiasts maintain that these disadvantages will presently be overcome by improved methods of chemical treatment. Thus far, no very satisfactory paper has been produced with more than a small percentage of cornstalk pulp. In newsprint paper, for example, cornstalk pulp has been used in connection with a considerable proportion of sulfite and soda wood pulp, which makes the total cost higher than ordinary newsprint, containing sulfite and ground wood. Prospects are brighter for the use of cornstalks for the manufacture of insulating board, wall board, and cork substitutes for linoleum manufacture.

The great quantities of sawdust, shavings and waste which accumulate in lumbering and the wood-working industries have long intrigued industrial chemists. Such material cannot ordinarily be used for paper, for it is commonly mixed with bark or is of undependable quality. Many efforts have been made to extract rosin and turpentine from stumps or to produce acetic acid, acetone and charcoal by destructive distillation of wood waste. The chemical and engineering difficulties that have been met have often been quite completely overcome. Yet these endeavors have sometimes been economically unsuccessful even when they were technically well-conceived. Those who are asked to support any attempt to find a use for any one of our major industrial wastes should remember that many previous efforts with such materials have failed for economic reasons. Waste materials remain waste materials, not because chemistry has been unable to produce valuable products from them, but because this has not yet been done at a profit.

Wood waste of the size of small cordwood may often be profitably distilled, to produce acetic acid and other products (p. 219). At present the most important use of sawdust and shavings is in the manufacture of wood flour, by a simple process of grinding. White pine is the

most valuable material. The United States consumes about 30,000 tons of wood flour each year. About half of this is used in the manufacture of linoleum. The darker and more resilient grades of linoleum consist of particles of cork dust embedded in a rubbery mass of oxidized linseed oil. Wood flour is preferred to cork dust in the brighter shades of tinted linoleum. About a quarter of the wood flour production is used in the manufacture of dynamite, and most of the rest is mingled with Bakelite and other synthetic resins, for the manufacture of molded products (p. 194).

Among the most persistent efforts that have been made to utilize wood waste are those attempting conversion of it into alcohol or food. In 1819 a French chemist, Braconnot, dissolved linen rags in cold concentrated sulfuric acid. He then diluted the acid with water, boiled the solution for about ten hours, neutralized it with lime, filtered off the insoluble matter and concentrated the liquid to a syrup. From this glucose (grape sugar) crystallized out! This discovery created intense interest and led to numerous attempts to convert cellulose into food, or at least into fermentable sugar for the production of alcohol. Enthusiasts had visions of the ragman delivering old shirts at the rear door of a chemical factory, while trucks were being loaded out in front with breakfast food or whiskey.

In several processes which were operated commercially for short periods, sawdust was converted into fermentable sugar by the action of hot, dilute sulfurous, sulfuric or hydrochloric acid. Arthur D. Little, Inc., some years ago, made extensive tests on a commercial scale, in which about sixteen gallons of 95 per cent alcohol were obtained from each ton of sawdust. Thousands of gallons of alcohol were produced by this process, but competition with other sources of fermentable sugar was too keen, and the process is not now in use.

Food and
Alcohol from
Cellulose

The most recent proposal is by Bergius, the inventor of the Bergius process for the production of motor fuel from coal (p. 160). He treats sawdust with "superconcentrated" cold hydrochloric acid, then removes most of the acid by evaporation in a vacuum, and spray-dries the resulting syrup. The sawdust is said to yield about 75 per cent of an impure glucose, suitable for cattle food, the remainder being promising as a binder in briquetting coal dust. A plant is about to go into operation (1930), fermenting glucose produced by this process. The question still remains, will it pay?

Prehistoric man wove coarse fabrics of leaves of grass or strips of pliant bark from the young branches of trees or shrubs. As his skill in the art increased, the plant material was reduced to finer and finer strips, previous to weaving. In the end, fabrics came to be woven of individual plant fibers, stripped from leaves, bark or stems of a great many different plants. By that time wool and hair were being twisted into threads, which were woven in the same manner as vegetable fibers. When the curtain of history rises on the earliest civilizations, mankind was already in possession of a great variety of textile materials.

Linen, which is woven from fibers stripped from the stem of the flax plant, is prehistoric. Cotton, woven from threads spun from the downy covering of the cottonseed, first became well known in India, in the Eighth Century before Christ. Chemistry has done little to improve the quality of either of these materials as they are furnished us by Nature. Linen is still prepared, as in prehistoric times, by soaking flax stems in stagnant water until gummy materials are dissolved by fermentation. Cotton receives a preliminary treatment with a very dilute, boiling solution of alkali, to remove waxy and resinous impurities. This is followed by bleaching.

It is in bleaching and dyeing that the first contributions of chemistry to the textile industry were made. As late as a century and a half ago linen and cotton fabrics were bleached by being spread out on grass in the sunlight, where they were kept moist by sprinkling with water during a period of many weeks. Finally, in 1787, chlorine, which had recently been discovered by the Swedish chemist Scheele, was used in bleaching. The process was thereby reduced from months to a few hours. Bleaching powder, which is made by absorbing chlorine in slaked lime, was soon afterward introduced, and until very recently was the principal bleaching agent in the textile industry. At present, liquid chlorine has largely replaced it.

In 1844 an English weaver, John Mercer, observed that when a strong caustic soda solution is poured through cotton or linen the fibers swell and become
Mercerizing gelatinous, and at the same time shrink very strongly. When the alkali is washed out the fabric is found to be of increased strength and more readily dyed than ordinary cotton or linen. Mercer made a fortune from this simple discovery, but failed to observe that cotton thread or yarn develops a bright luster if it is stretched or held under tension while wet with the caustic soda solution.

Cotton in its natural state is seen under the microscope to consist of flattened, twisted ribbons. The alkali causes these to swell to round threads, and the tension or stretching takes out the twists and gives the threads a smooth cylindrical surface. This is responsible for the luster. The product is called mercerized cotton. It is still cellulose, more highly hydrated* as a result of the treatment with alkali, but not seriously altered chemically.

Silk has been an important textile fabric in China for at least forty centuries. From China the industry spread to other parts of the Far East. Silk-growing and silk-weaving were introduced into Europe about the year 550,

* *Hydrated*, chemically combined with water.

and there attained a high degree of technical perfection a thousand years before there was any science of chemistry. The chemist has merely introduced methods for reclaiming waste silk and somewhat better methods than were previously known for purifying raw silk and for dyeing.

Silk and
Rayon

Silkworms turning mulberry leaves into silk were a challenge to chemists to do the same. The leaves were the subject of many experiments, which finally led to the invention of rayon. Nevertheless rayon is cellulose, whereas silk is a nitrogenous compound, synthesized by the silkworm from the non-cellulosic ingredients of mulberry leaves.

The customary forms of cellulose used for the production of rayon are bleached sulfite pulp of high alpha-cellulose content and bleached cotton linters, or sometimes a mixture of these. There are four chief processes. The oldest of these is that developed by Count Chardonnet, in France, about 1883. Cotton was treated with a mixture of nitric and sulfuric acids, forming nitrocellulose (p. 181). This was dissolved in a mixture of alcohol and ether and forced through fine openings, producing lustrous threads, which hardened by evaporation of the solvent. The threads were then denitrated by treatment with calcium sulfide or some other reagent, which caused them to revert to ordinary cellulose.

Nitrocellulose
Rayon

It took seventeen years to perfect the Chardonnet process, from the earliest experiments to the moment the product was a commercial success. Methods for solvent recovery had to be worked out and there were numerous chemical and mechanical difficulties to be overcome. New types of spinning and weaving machinery, and new methods of dyeing and finishing had to be developed. Then, just as Chardonnet rayon was winning favor, the viscose process came forward and won the largest part of the market. Considerable Chardonnet rayon (now

often known by the trade-name Tubize) is produced in the finer deniers (filament sizes), on account of its having a somewhat greater strength than viscose rayon.

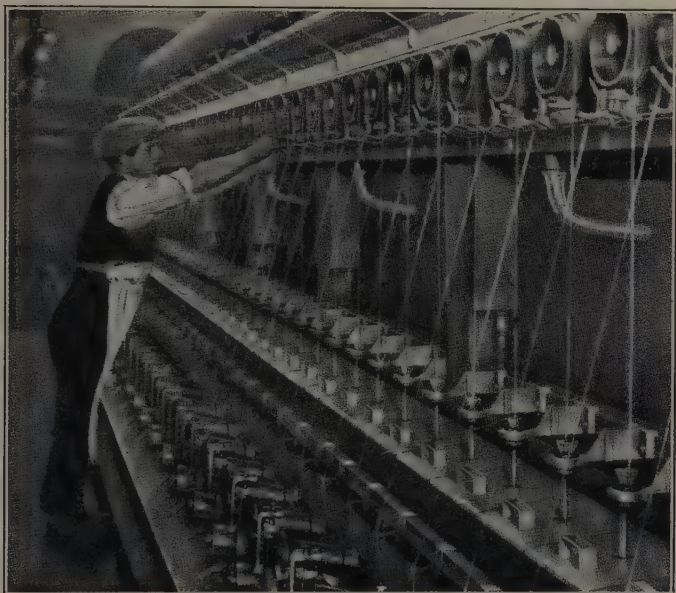
Viscose rayon is based on a discovery of the English chemists Cross and Bevan, in 1893. They observed that pure cellulose, when treated with concentrated caustic soda, then with a limited amount of carbon disulfide, is slowly converted into a product that will dissolve in water or dilute caustic soda, forming a viscous solution that may be spun into threads. By treatment with dilute acids these threads are reconverted into cellulose, with chemical properties not greatly different from those of the original raw material. The product is called viscose.

The viscose process was not an immediate success, and in 1903 the American rights were sold at public auction for \$25,000. Today they would be worth millions. The production of viscose was established on a commercial scale in France by 1900, and in Great Britain and America by 1907.

As practiced today, the production of viscose rayon is an extremely complicated process, in the development of which vast sums needed to be expended. The sulfite wood pulp used as a raw material needs to be purified by an elaborate chemical treatment. The purified stock is steeped in caustic, pressed to a definite content of caustic, shredded, aged, treated for a definite length of time with a definite amount of carbon disulfide, then dissolved in water. The solution thus formed is ripened at a definite temperature until it acquires a definite viscosity, is filtered, deaerated, and formed into filaments and spun into threads from bobbins or centrifugal pot-spinning machines. The finishing process, in the pot-spinning method, includes in succession the operations of steaming, reeling, washing, drying, desulfurizing, washing, bleaching, scouring, washing, centrifugal drying, hot room drying, humidifying, grading, knotting, and packing. Opera-

tions of dyeing, weaving, printing and finishing then follow. The wonder is that rayon is not as costly as silk, which, when it first became known to Europeans, was worth its weight in gold.

Viscose in the form of transparent sheets, used for wrapping candy, cigars, and food, is known as cellophane. Its production is now a great industry, capitalized at millions of dollars. Viscose sausage casings and viscose hair,



Courtesy of Whittin-Kohorn Co.

POT SPINNING MACHINES IN A RAYON FACTORY

wool, straw and ribbon are now widely used. Viscose wool has a natural kink which permits it to replace real wool or to be mingled with real wool in clothing. Hollow, air-filled viscose yarn imitates silk very closely.

A third type of rayon is made by the cuprammonium process, in which purified cotton linters
Bemberg are dissolved in a solution of copper hydroxide and ammonia, then formed into filaments by forc-

ing the solution through fine openings into a coagulating bath containing dilute acid. The best-known product of this class is sold under the trademark Bemberg. It has advantages for certain applications, such as rayon warp for garment linings; but it is produced in much smaller quantities than nitrocellulose or viscose rayon.

The preceding forms of rayon are all nearly pure cellulose. Cellulose acetate rayon, by contrast, is a different substance, made by treating purified cotton linters with acetic acid and acetic anhydride, in the presence of a catalytic agent. The cellulose acetate is precipitated, purified, dried, dissolved in acetone, and formed into filaments, which are spun into thread. The product may be weighted and improved in appearance with tin salts. The world's production of acetate rayon was 9,000 tons in 1929, and is growing rapidly. Three large new plants came into operation in that year in the United States. Trade names are Lustron, Celanese, Rhodiaceta, Acele and Chacelon.

Acetate rayon is of high luster, and considerable strength, and may be spun in filaments of unusual covering power for unit weight of material. It calls for special methods of spinning, weaving and dyeing, and is more readily injured by a hot iron, when garments are pressed, than any of the other three sorts of cellulose rayon.

Rayon has recently been our most rapidly expanding organic industry. In 1919 the United States produced 4,500 tons of rayon; in 1924 this had become 19,000 tons; and in 1929 about 65,000 tons. Over 80 per cent of the present production is viscose rayon. The world production of rayon, in 1929, was about 200,000 tons.

Rayon has always suffered from the disadvantage of being weakened by being wet, but the best modern products lose only somewhat more than half their strength when wet and regain it on being dried. The Lilienfeld

**Cellulose
Acetate
Rayon**

**Rayon
Production**

viscose process (1929), stretch-spinning in a strongly acid bath, produces rayon thread with practically the strength and elasticity of silk. Rayon may be delustered by incorporation of minute air bubbles, a few tenths of a per cent of petroleum jelly, or by a surface treatment with zinc sulfate or magnesium sulfate. The popularity of this material is surprising when we consider that rayon first won its place through its luster. Transparent rayon velvet has recently appeared, and rayon linings for men's



Courtesy of the Rayon Institute of America

WARPING MACHINES IN A MODERN RAYON FACTORY

clothing. Though production of rayon has at present nearly overtaken demand, the constant development of new uses is to be expected. This attractive product of the chemist's art has been chiefly worn by the feminine half of humanity.

When cotton is treated with a mixture of nitric and
Nitrocellulose sulfuric acids, under definitely controlled
Explosives conditions of temperature and concentra-
tion, it is converted into a cellulose nitrate, which deto-

nates with great violence when struck on an anvil. The Swedish chemist, Nobel, discovered in 1867 that this material, otherwise known as "guncotton," dissolves in warm nitroglycerine, which is itself an explosive. The result is a gelatinous mass, which is the basis of modern smokeless powders. Smokeless powder and guncotton belong to the relatively slow-burning class of explosives known as propellants, which are used to fire projectiles from guns. Quick-burning, high explosives, such as TNT, would burst the gun.

Nobel devoted more than twenty years to research with explosives, in the course of which he invented dynamite (nitroglycerine, absorbed in a porous material, such as wood flour). He also learned how to detonate explosives with the aid of caps containing mercury fulminate, a near relative of the compound which so nearly put a premature end to Liebig's experiments (p. 39).

Nobel's work made it comparatively safe to employ nitrocellulose and nitroglycerine in blasting. By his contributions to the art which incidentally made possible war of the sort that has recently been waged, he accumulated a great fortune, which enabled him to offer generous prizes for the advancement of world peace. Of course civilization could hardly spare the cellulose nitrate explosives, for their military uses are quite overshadowed by their importance in clearing land of stumps, in quarrying rock, mining coal, and in executing such engineering feats as the Panama Canal or railroad tunnels through mountain ranges.

Other important products derived from cellulose are the cellulose nitrate and cellulose acetate plastics, films, and lacquers. These are discussed in the following chapter. Wood distillation is discussed on page 219.

CHAPTER XIV

SYNTHETIC PLASTICS

UNTIL very recently many of the conveniences of life were laboriously fashioned from wood, bone, horn, or stone by a process of sawing, whittling, chiseling, or turning on a lathe. Today these materials have largely been replaced by plastics, namely, products that can be shaped by pressure. A business man sits at his desk, wearing plastic-framed spectacles, writing with a plastic-molded fountain pen. He answers a telephone, holding a receiver and speaking into a mouthpiece made of plastic material. The buttons on the front of his coat, his pipe-stem or cigarette holder, ash tray, ink-stand, paper knife, ruler, transparent lamp shade, the keys of his adding machine, and molded electric fixtures on the walls—are all made of synthetic plastics, shaped by pressure. Furniture molded from plastic materials will come next. Fifty years ago all of these things would have had to be made from very different materials and by much more costly processes.

Plastic materials are *colloids*. By this we mean that they consist of huge aggregates of molecules, of indefinite or unknown molecular weight, and generally of unknown constitution. Colloidal particles are to ordinary molecules somewhat as snowballs to individual snowflakes. The largest colloidal particles, though relatively huge in comparison with molecules, are still too small to be seen with the most powerful microscopes.

In synthesizing plastic substances in the laboratory the

problem is to construct colloidal aggregates from simple molecules. Usually the reaction has not proceeded very far on the way toward the colloidal realm until we lose track of it entirely. The chemical nature of the final product is then shrouded in mystery. Nevertheless, we may find that product useful. Examples of natural col-



Courtesy of the Bakelite Corporation

PLASTICS IN THE OFFICE

Here synthetic plastic materials appear in the telephone, pencil, smokers' accessories, electric lighting fixture, and clock.

loids of unknown or incompletely determined chemical structure are resins, bitumen, starch, cellulose, and clay.

Man's first plastic material was clay. It had the valuable property of becoming permanently rigid and non-plastic on being heated. Objects molded from clay could be made to retain their form for all time, by firing them in a furnace. The pottery of prehistoric man has outlasted his very bones.

Natural Plastics

The earliest historical races also molded small objects

from resins, waxes, pitches, and bitumen. A lion's head, molded of bitumen and covered with sheet copper, was discovered in Mesopotamia a few years ago, in deposits dating from about 3500 B.C. Bitumen is still used in molding today, commonly in admixture with rubber or a little linseed oil.

From the prehistoric Bronze Age down to the present time, beads and other ornaments have been fashioned from amber, which is a fossil resin, chiefly found on the shores of the North Sea. Amber is usually shaped by cutting, but it becomes soft enough to be molded if heated cautiously. At present it is being displaced by cheaper synthetic resins that are very similar in appearance and properties to amber itself.

The most important natural plastic resin is shellac, which is secreted by the lac insect on twigs of certain trees in Siam and neighboring parts of the Far East. It is the chief constituent of sealing wax. It is still used as an electrical insulator in situations in which it is not likely to be softened by heat. Phonograph records are often molded of a plastic mixture consisting largely of shellac.

To the natural plastics, chiefly of resinous nature, which have just been mentioned, organic chemistry has now added a number of synthetic plastics, of the most varied characteristics. The longest known of these are derived from

Pyroxylin Plastics

pyroxylin. Pyroxylin itself is nitrocellulose, made by the action of nitric and sulfuric acid on cotton linters or purified wood pulp, under more moderate conditions of concentration and temperature than those that result in gun-cotton (p. 182). It has the fibrous structure of the raw material from which it is derived. Yet in the presence of camphor and a little alcohol the fibers swell and dissolve, giving a dough-like mass, which can be rolled into sheets or extruded through a die to form hollow tubes. This discovery was due to two American chemists named Hyatt,

in 1869, who based their work on the experiments of some previous English investigators.

When the alcohol has been removed by evaporation from the plastic mass, prepared as described above, the product is a horny solid, tough, flexible and strong. It may be readily cut, sawed, stamped, drilled and machined. More important yet, it softens and becomes fully plastic at temperatures just above the boiling point of water, and may be molded into complicated shapes. Hollow toys are made by blowing steam between sheets of the plastic, placed face to face in a mold. Non-shattering glass consists of a sheet of pyroxylin between two sheets of glass.

The pyroxylin plastics, when not blended with other materials, are quite transparent and almost completely colorless. They may be given a great variety of transparent and opaque colors by incorporating dyes and pigments with the plastic mass. The tints and luster of pearl, jade, tortoise shell, horn, ivory and onyx may be very exactly reproduced. Trade names are Celluloid, Xylonite, Lucite, and Pyralin. The United States produced about 15,000 tons of pyroxylin plastics, in 1929.

As late as 1922, automobiles were finished with varnishes and enamels containing linseed oil and other oils that dried by a slow process of oxidation.

**Pyroxylin
Lacquers**

The time required to refinish an automobile body might be as long as three weeks.

Today this has been reduced to a few hours, by the development of pyroxylin lacquers that dry by evaporation of a volatile solvent.

A satisfactory automobile lacquer must not only be quick drying but tough and flexible, not easily scratched, resistant to sunlight and reasonable degrees of heat, resistant to water, oil, gasoline and dilute alcohol, of high gloss, attractive color, and adhesive to metallic surfaces. These requirements were first obtained in a fair degree when means were discovered for producing pyroxylin

solutions of high pyroxylin content yet of sufficiently low viscosity to be applied by spraying. By the addition of colored pigments the lacquer could be rendered opaque and more resistant to sunlight and abrasion. Imitation leather is usually pyroxylin-coated fabric. About 40,000,000 yards were produced in the United States for automobile tops and cushions, in 1928.

The first solvent used in pyroxylin lacquers was amyl acetate, which was at that time prepared almost exclusively from fusel oil, a by-product of alcoholic fermentation (p. 267). At present, it is largely synthesized from pentane, which is one of the components of natural gas (p. 137). A number of other esters and alcohols have been developed for use as pyroxylin lacquer solvents, generally in admixture with volatile hydrocarbons, derived from petroleum or coal tar. These serve to thin or dilute the solution. Among the new solvents are butanol, or normal butyl alcohol, which is produced on a large scale by the fermentation of corn mash (p. 268), and glycol esters, derived from ethylene (p. 142).

The sudden widespread use of these pyroxylin lacquers has had important effects on the whole organic chemical industry, particularly in the United States. In the eight years from 1921 to 1929, the production of non-coal tar chemicals in the United States increased about thirteen-fold, namely from 10,500 to 140,000 tons annually. About two-thirds of the present total represents pyroxylin solvents. Meantime the production of coal-tar chemicals has increased less than three-fold, namely from about 25,000 to about 66,000 tons annually.

We shall have frequent occasion to note with what startling rapidity new chemical products are now taken over into industrial practice and developed on a large scale. Chemical inventions that are worth while need no longer wait weary decades for their application. Engineering facilities for their production in quantity, chemi-

cally trained hands and brains for their development, and financially powerful interests for their support are everywhere at hand.

The pyroxylin plastics, just described, suffer from the great disadvantage of being extremely inflammable. If not handled carefully, they are apt to result in serious fires. This defect led to the commercial development of the cellulose acetate plastics.

**Cellulose
Acetate
Plastics**

Cellulose acetate is usually produced by the interaction of a mixture of acetic acid, sulfuric acid and acetic anhydride on highly purified cotton linters or other pure cellulose materials. It can be dissolved in various organic solvents, such as acetone, alcohol and many esters, and with suitable plasticizers may be converted into sheets, films, lacquers or textile fibers. Its use as a plastic in competition with the pyroxylin plastics has been retarded, due principally to its high cost and the lack of suitable plasticizers and solvents at an economic price. These difficulties have now been largely overcome, and many new solvents and plasticizers have been discovered that assure the development of cellulose acetate plastic films and lacquers comparable with those that have been made with pyroxylin. A recent plastic of the cellulose acetate group is Lumarith. This was developed by the Celluloid Corporation, which also pioneered the development of the cellulose nitrate plastics. It is produced in a wide range of colors and mottled effects, and is rapidly finding a place in industry for decorative electrical equipment, lamp shades and various other uses in which color effects have an appeal.

In 1885 an American chemist observed that casein, which is the chief ingredient of the clot or curd of curdled milk, may be hardened by formaldehyde and some other substances, resulting in the production of a horn-like solid. This discovery was improved upon in Europe, and casein plastics

**Casein
Plastics**

of various trade names were placed on the market, whence they were imported extensively into the United States until the enactment of the tariff law of 1922 so increased the cost that pyroxylin plastics were substituted for them.

American manufacturers immediately entered the field and are producing material in a wide range of colors from black to the most brilliant hues. Horn, ivory, jade, coral,



Courtesy of the Karolith Corporation

ARTICLES MOLDED FROM A CASEIN PLASTIC

The casein plastic here shown is based on research carried out at the Mellon Institute, in Pittsburgh. Recent achievements include the development of casein plastics that are practically transparent or that are sufficiently plastic to acquire a polish in the mold.

turquoise, amber, amethyst and tortoise shell are realistically imitated.

Casein plastics are relatively cheap, very strong and completely non-inflammable. They are difficult to mold, since they generally do not become completely plastic even when softened by immersing in hot oil or a mixture of glycerine and water. For this reason they are usually worked with tools and require a final polish, which can be obtained by tumbling as well as buffing. By contrast,

the natural and synthetic resins may be formed in polished molds, and leave the molds with a highly finished, glossy surface.

The casein plastics also shrink or warp somewhat on seasoning or on exposure to moist air; hence objects cannot be molded from them to the precise dimensions that are possible with some other plastics. For this reason they are applied chiefly in the manufacture of small objects of comparatively simple shapes, such as buttons, beads, pens, pen holders, sheets, rods and tubes. Yet more complicated shapes are now being produced as a result of recent research. Trade names are Galalith, Karolith and Erinoid.

PHENOL-FORMALDEHYDE RESINS

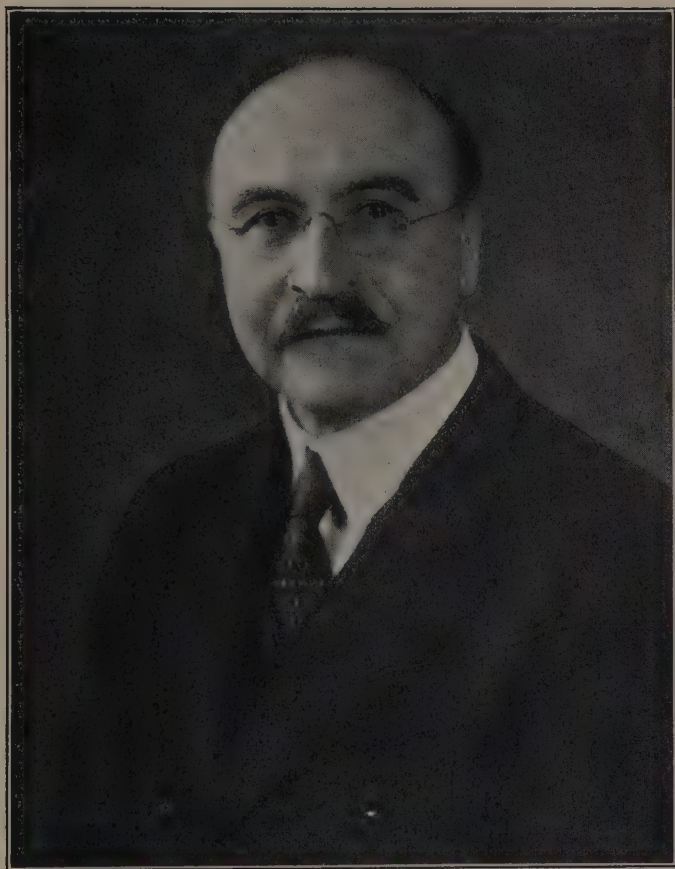
The synthetic plastics just described, like the natural resins, waxes, and bitumens, are all softened by heat.

Articles molded from them therefore need to be carefully safeguarded from temperatures above the boiling point of water if they are not to collapse into shapeless masses. Industry had need of materials that resembled man's earliest plastic, clay, in being hardened, rather than softened, when exposed to moderately high temperatures. This result was finally achieved with plastics made by the condensation of phenols with aldehydes.

The first observations in this direction were those made by Baeyer, the discoverer of synthetic indigo, in 1872. He found that sticky, resinous masses were often produced when formaldehyde reacted with phenol. This was exasperating, for the organic chemist of those days was chiefly interested in products that he could purify by redistillation or recrystallization. One that was non-volatile and refused to crystallize seemed very unpromising grist for his research mill.

Nevertheless, a number of different workers attempted

Baekeland's
Researches



Courtesy of the Bakelite Corporation

LEO H. BAEKELAND

Dr. Baekeland developed Bakelite, the first useful phenol-formaldehyde plastic, by years of exhaustive research. He is also the inventor of Velox photographic paper.

to develop something useful from these resins. The great difficulty was in controlling the reaction sufficiently to secure a product of uniform quality. Sometimes it was crystalline, at other times soft and sticky, and again hard and infusible.

Leo H. Baekeland, an American chemist of Belgian birth, was the first to succeed in controlling these mysterious reactions. After a number of years of research, first published in 1909, he began to produce commercially a resin which could be melted and incorporated with fillers, and which would quickly alter, when heated under pressure, to produce a hard, insoluble, infusible mass.

When formaldehyde is combined with phenol in approximately the proportions of their molecular weights, **Bakelite** in the presence of ammonia or a very small amount of an *alkaline* catalyst, the reaction is extremely vigorous, and becomes violent unless carefully controlled. The product continues to condense, giving off water until it reaches a stage at which it becomes brittle enough to grind. This brittle resin (Bakelite A), is fusible and soluble in alcohols and acetone, but insoluble in benzol and other hydrocarbon solvents. On further heating, the chemical alteration of the material continues, and Bakelite A goes over into Bakelite C, which is the finished infusible, insoluble material. This is called the one-stage process.

The next improvement in the production of phenol-formaldehyde resins was in condensing phenol, in the presence of an *acid*, with a smaller proportion of formaldehyde—approximately one-half mole of formaldehyde for each mole * of phenol. This produces a brittle resin, termed Novolak, which is not hardened by heat. Yet when this product is mixed with formaldehyde in the form of dry hexamethylene-tetramine and a basic catalyst (lime or a lime salt), then heated under pressure, it goes over

* A mole of any substance is as many grams as there are units in its molecular weight.

into Bakelite C. This is the two-stage process. The Bakelite of commerce is produced in this way.

The fact that the soluble, fusible Bakelite A is rendered insoluble and infusible by heat suggests a number of applications. The resin may be dissolved in a solvent and applied to metals as a lacquer. When the solvent has evaporated the lacquered object is baked. This fixes the coating. Protective, transparent Bakelite lacquers for brass and copper and insulating lacquers for fine wire are very widely used.

Lacquers and Laminated Products



Courtesy of the Bakelite Corporation

BAKELITE PRODUCTS

Thousands of accessories, industrial and domestic, are now produced in a single operation from Bakelite molding material. The new telephone and the 25-pound insulator (center) are typical; also the automobile distributor head (lower left).

Heat-hardened Bakelite cements are used to attach glass to brass in manufacturing electric light bulbs. Paper, impregnated with Bakelite varnish, is compacted and

hardened into radio panels under heavy pressure, in steam-heated presses. Canvas, similarly treated, with layers criss-crossed, may be formed into solid blocks that are exceedingly tough and strong. The timing gears of most automobiles and silent gears for light and heavy machinery of all kinds are made of this material. Trade names of such laminated products are Textolite, Celoron, Delecto, Formica, Phenolite, Fibroc, Spaulding, and Synthane.

Transparent Bakelite resins of an attractive light amber color are in common use in pipe-stems, cigarette holders, and beads. Clouded and multi-colored resins effectively imitate semi-precious stones. Such products are odorless, tasteless and resistant to moisture, oil and solvents.

By far the widest use of phenol-formaldehyde resins is as molding powder, intermingled with wood flour, asbestos or some other inert filler. The purpose is not only to lower the cost of the molded product but reduce the amount of shrinkage on cooling, and increase the mechanical strength. By choosing a resin having the right degree of fluidity at the molding temperature and intermingling it with the right proportion of a filler, objects may be molded to accurate dimensions. They leave the molds with polished surfaces, needing no further finishing. Trade names for such molded products are Bakelite, Textolite, Durez and Celoron.

Molded phenolic resin products have a multitude of uses, dependent on their hardness, toughness, and electrical insulating qualities: Telephone mouthpieces and receivers, radio accessories, switch plates, light sockets, fountain pens, instrument cases, tool handles, and type-writer space-bars. The material resists all ordinary solvents and most chemical reagents, the most important exceptions being alkalies and strong acids. It resists heat up to temperatures well above the boiling point of water, unless it has been mixed with a filler that is readily decomposed by heat. The United States, in 1929, produced

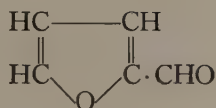
Molding Powders

about 15,000 tons of solid phenolic resins. This does not include phenolic resin lacquers.

Durez is a phenol-formaldehyde resin, made by a modification of the one-stage process, developed by another American chemist, Harry M. Dent. He succeeded in simplifying the procedure, so that objects which needed to be produced cheaply in great quantities could be molded from phenolic resins. Articles of the most diverse kinds are fabricated of Durez in bright colors, of accurate dimensions, and at very low cost.

PHENOL-FURFURAL RESINS

Other aldehydes have been used instead of formaldehyde, and relatives of phenol instead of phenol itself, in the preparation of synthetic resins. Of especial interest are the resins made by condensing phenol with furfural, which is an aldehyde of the formula



Furfural is readily obtained from oat hulls, corn cobs, or similar material, by distillation with dilute acids, preferably (in the case of corn cobs) with such an amount of acid as will just neutralize the alkaline substances that the raw material contains.

The development of commercially useful phenol-furfural resins met many difficulties and called for years of painstaking research, as in the case of the phenol-formaldehyde resins, just discussed. Experience gained with the latter did not prove very helpful when furfural was substituted for formaldehyde, for the two aldehydes are structurally very different. The work that finally led to the production of a useful new group of resins was carried

out in the laboratories of the Stokes and Smith Company, in Philadelphia, in the years just following 1920.

It was first noted that phenol and furfural, when brought together in approximately equal quantities in the presence of a trace of acid, react violently to produce a rubbery or gelatinous product. To obtain a resin of the fusible type it was necessary to use an excess of phenol, with a small amount of furfural and a trace of acid. After a few hours at room temperature the unchanged phenol was removed by distillation or otherwise. The product was a fusible mass which became infusible on prolonged heating under pressure, but the transformation was too slow to be commercially attractive. Better results were obtained when hexamethylene-tetramine was added to the mixture to combine with the excess of phenol, or when phenol-furfural resin or furfural itself was incorporated with the reactants in the preparation of resins of the phenol-formaldehyde group. Black resins were thus obtained, which were claimed to be superior to the phenol-formaldehyde resins then made in plasticity and resistance to decomposition by heat.

Another successful procedure is to heat furfural with somewhat more than its own weight of phenol, in the presence of a very small amount of a basic catalyzer, such as potassium carbonate, under conditions such that the water produced in the reaction escapes, while any phenol and furfural which may be volatilized are condensed and returned. The product is a fusible resin, which is slowly transformed by heat and pressure into an infusible product. Again the transformation proves to be too sluggish unless hastened by the addition of hexamethylene tetramine, when a molding powder is to be prepared. For the production of lacquers or laminated products formaldehyde or furfural may be added to hasten the transformation into the infusible form.

**The Acid
Process**

**The Basic
Process**

By preheating the fusible resin to temperatures just below its transformation point, then injecting it into the mold through a hot gate and applying pressure, transformation into the infusible form can be accomplished in a few seconds. The mechanical arrangements by which these operations were carried out were an important new development in molding technique, and did much to lower the cost of manufacture of molded products. Resins produced by the neutral or alkaline processes are a light brown, those produced by the acid process a lustrous jet black.

The most spectacular application of the new resins is in the production of stereotype plates for printing. These are made by forcing the melted resin against the surface of a heated metallic matrix carrying depressions corresponding to the elevations of the printing surface. The plate thus made needs to be ejected hot from the mold. The phenol-furfural resins were the first to be developed that could stand this treatment without being blistered by the escape of gases. Printing plates so made have scarcely ten per cent of the weight of copper electrotypes, and have already been widely used in printing magazines in black and in colors.

The future of these resins depends on the price of furfural. There is no limit to the supply of this material, for the United States annually produces about

	Approximate Percentage of Furfural
4,000,000 tons corn cobs.....	20
800,000 tons cottonseed hulls.....	12
375,000 tons oat and rice hulls.....	10-12

By the work of American chemists during the ten years just following 1920, the price of furfural has been reduced from thirty dollars to ten cents a pound. The furfural resins make excellent binders for wood, and it has been claimed

**Furfural
Prices**

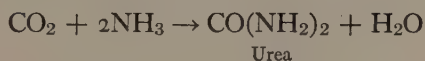
that synthetic lumber, made from sawdust with furfural resins as a binder, only awaits the production of furfural at about half its present price.

OTHER SYNTHETIC PLASTICS

The General Electric Company has developed Glyptal resins, which are made by the interaction of phthalic anhydride and similar compounds with glycerol. These resins are of a pale yellow color, and less subject to darkening by exposure to light than most of the resins of the Bakelite group. Their most important application is as insulating material in electrical equipment, in situations in which arcing is likely to occur. An arc struck across other resins is apt to leave a conducting trace of graphite. The Glyptal resins, like the Bakelite resins, are hardened by heat, but at somewhat higher temperatures acquire some degree of plasticity, perhaps comparable with that of leather. They are dissolved by a wide range of solvents, including even dilute alcohol and mixtures of alcohol and benzene. Such solutions may be employed as lacquers, which are hardened by a baking process after drying by evaporation of the solvent. If they carry linseed oil they may even be cured below the temperature of boiling water.

There are still other synthetic plastics. Urea and thiourea react with formaldehyde to form colorless, glassy, transparent solids, often called organic glasses. These may be brilliantly colored, are less easily broken than ordinary glass, are more resistant to water than the cellulose acetate and casein plastics, and have the advantage of transmitting not only visible light but the health-lending ultra-violet light of the sun. At present, however, there is difficulty in fabricating very large sheets of this material, and it scratches much more readily than glass. Trade names are Pollopas and Beetle.

It is interesting to note that the plastics of this group are derived from urea, the first product of plant and animal life to be produced in the laboratory from non-living materials, just a century ago. We wonder with what feelings those who denied the possibility of such a synthesis would view the manifold synthetic organic industries of today. The urea used in the preparation of the organic glasses may be produced by the direct union of carbon dioxide and ammonia, under a pressure of 1000 pounds to the square inch, at about 150° C., in the presence of a catalyzer:



Wöhler's synthesis of urea was never of industrial importance, and even the more recent synthesis of urea from calcium cyanamide (p. 126) is challenged by this new achievement.

Even this does not complete the list of synthetic plastics used today. Schellit is the trade name of a transparent, colorless phenol-formaldehyde resin, which differs from most other members of its class in not being darkened by light.

**Cumarone
Resins**

The cumarone resins are fusible, black solids, produced by the action of sulfuric acid on certain ring compounds present in coal tar distillates. Thousands of tons have been manufactured, particularly in Germany.

Synthetic resins are also often intermingled with natural resins or rubber. Hard rubber or ebonite is described on page 205. Cases for storage batteries are now frequently molded of mineral rubber (p. 208), mixed with waste cotton fiber. Transparent, plastic masses of vulcanized rubber have been produced. And just below the industrial horizon and still in the experimental stage are yet other synthetic resins, such as those derived from vinyl acetate or from styrene. Some of these will doubt-

less be found to possess distinctive properties, fitting them for special uses of their own. The chisel, saw, and gouge are rapidly being displaced as implements of serious manufacture, and give place to the steam-heated press.

CHAPTER XV

THE CHEMIST IN CONTROL

IN THE first part of this book we related the steps by which a knowledge was gained of the inner structure of the molecules of organic compounds.

**Synthesis vs.
Adaptation**

Based on that knowledge, the ability was acquired to synthesize many complicated molecules from simpler ones. The result was a great group of industries, growing daily in importance, that begin with calcium carbide or with simple compounds present in natural gas, petroleum and coal tar. From these, proceeding step by step, adding atom to atom, they elaborate the amazingly complicated molecules of dye-stuffs, perfumes or medicinals. These, the synthetic organic industries, furnish the best examples of the methods by which creative minds in the chemical realm bring compounds into being which duplicate those produced by Nature, with many others that Nature never knew.

Still, chemical synthesis has not yet produced any of the major products of plant and animal life, on which we depend for food and clothing. Cellulose, cane sugar, starch, and proteins have never been produced by synthesis from simple compounds in the laboratory. Edible fats and oils have been thus synthesized, but we are still far from doing this cheaply enough to compete with living cells. We can produce alcohols, simple organic acids, aldehydes, glycerol and many other products from calcium carbide or even from carbon dioxide; but the question is ever present whether some micro-organism, living unnoticed under our very noses, may not do better.

The industries that turn over the greatest mass of raw materials are those in which such complex natural products as starch, fats, cellulose, wood, coal and petroleum are decomposed into products that are chemically simpler. Organic chemistry may best serve industry by synthetic efforts, in which complex organic compounds are built up from simple beginnings, plus adaptive efforts, in which compounds produced by living plants and animals are modified to our use. Many great industries are based on such compounds. They served mankind for thousands of years and reached a high state of perfection before there was any science of chemistry.

Now that we know something of the chemical nature of the raw materials on which these industries are based, our duty is to see that they are intelligently used. Is the synthetic skill of Nature being used to best advantage, by careful selection and gradual improvement of the species and races of plants and animals that we employ? Are her products being wastefully exploited or intelligently conserved? Are age-old practices in industries that are based upon her creations scientific and sensible, or the result of superstition, tradition, prejudice, and misunderstanding?

Many industries still operate in directions suggested by primitive methods, without important changes in principle as a result of the development of organic chemistry as a science. They have merely grown large. Thus, though chemistry has discovered methods for purifying sugar that are superior to any known in ancient times, and though a modern sugar factory in a single day probably produces as much sugar as the early civilized world produced in the course of many years, still the essential process—precipitation of impurities by the addition of lime, evaporation of the liquid to crystallization, and separation of the sugar crystals from uncrystallized molasses—is that of ancient days.

**Antiquity of
Some Organic
Industries**

In the manufacture of paper we have introduced the use of chemical substances that were never employed until very recently, and we have enormously expanded the output of paper; but we have not greatly changed the essential process as practiced for centuries, which consists in separating the fibers of plant material from each other without altering them chemically, then felting them into a coherent mass, which is compacted by pressure and rendered impervious by the addition of clay or other fillers. There is very little chemical science in such operations as these. Until very recently we did not know, in any accurate way, just what the encrusting and cementing materials are which bind the fibers together, as they are furnished us by plants. By a lucky guess it has been found that calcium bisulfite, caustic soda, and some other inorganic chemical compounds are effective in softening and separating the fibers.

So, when we observe paper machines that turn out sheets 25 feet wide, or that produce 1,000 to 1,200 running feet of paper a minute, and when we meet with tanks 18 feet in diameter and 50 feet high, of concrete lined with vitrified brick, and taking perhaps 400 tons of bisulfite liquor and wood chips at a single charge, we are not witnessing triumphs of chemistry but of engineering. Chemistry is a mere servitor of the paper industry, not its creator.

The part that the chemist plays in the manufacture of paper, sugar, starch, casein, meat products, vegetable oils, and glue is similar to that played by the banker or lawyer in the service of these industries. His duty is to control, survey, protect and advise. Chemistry creates nothing in these products that was not created by the living plant or animal, in admixture with or loosely combined with other substances. The chemist furnishes methods of separation and methods of analysis. He checks the quality of raw materials and finished products. He supports the engineer in the development of new materials for plant equip-

Control vs.
Research

ment. He aids the management in operation and control. That is apparently all.

There is, however, always the chance that the chemist may develop some process that is quite revolutionary, or that he may create synthetic products to displace the natural products from some of their ancient uses. The organizations that benefit from such achievements are those that employ organic chemists not merely to control production but to engage in deep-delving research. The superficial aspects of industry are its temporary aspects.

Paper-making has already been discussed. Now for some other industries that the organic chemist has aided less by his synthetic skill than by his services in controlling operation. All of these are feeling the stimulus of new methods and new points of view, created by chemists whose work extends beyond that of mere control.

RUBBER

Rubber is a hydrocarbon, $(C_5H_8)_n$,* which is produced as a milky fluid called rubber latex by a number of tropical plants of widely different species. Its extraordinary properties have been known and appreciated in the New World for many centuries. In the forest-covered ruins of Chichen Itza, in Central America, a ball of solid rubber about ten inches in diameter was recently discovered, that was put in play by children of long ago. The outer portion of this ball had of course been ruined by oxidation, but within was a small mass that still retained its elasticity after a period of perhaps eight centuries. Rubber was in familiar use in these countries in the time of the Spanish conquistadores, who were taught by the natives to water-proof their capes, by dipping them in rubber latex.

* The subscript n indicates that the rubber molecule is an undetermined or indefinite multiple of the group C_5H_8 .

In former decades rubber came very largely from the wild rubber trees of the Congo and Amazon basins. At present over 95 per cent is plantation rubber, produced on great cultivated estates. Over 6,000 square miles have been planted, chiefly in Malaya and the East Indies. In 1928 the Ford Company began the development of great rubber estates in Brazil, in the hope of producing rubber so cheaply as to encourage the development of many new uses.

Rubber Production

The United States uses over two-thirds of the world's rubber. A large part of this is worked up in the one city of Akron, Ohio. In 1928 the crude rubber contained in manufactured articles produced in the United States amounted to over 480,000 tons, of which over 416,000 tons were used for tires. The total value of rubber manufactured products was about \$1,100,000,000, and of tires alone, about \$850,000,000.

The milky rubber latex collected from incisions in the bark of the tree, is caused to clot or coagulate by adding small amounts of acetic acid or in other ways. The clotted material may be separated from the watery serum, washed, and rolled out into sheets, in which form crude rubber is now usually imported.

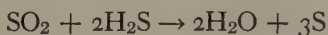
Vulcanizing

In 1839 Charles Goodyear, an American inventor, discovered that when crude rubber is heated with a small proportion of sulfur it becomes tougher, stronger and less sensitive to heat. This was the first vulcanizing process. The discovery was put to immediate use in the improvement of rubberized fabrics, which were even then being made, in spite of the fact that unvulcanized rubber is soft and sticky in summer and almost as stiff as sheet iron in winter.

With a larger proportion of sulfur, hard rubber (ebonite) is produced, which has been widely used as an electrical insulator and for molded products, such as fountain pens, telephone mouthpieces and battery boxes. From

many of its former uses it is now being displaced by the synthetic resins described in the preceding chapter.

Much of the rubber of commerce is still vulcanized or cured by heating with sulfur. Cold vulcanization usually employs vapors of sulfur monochloride, S_2Cl_2 , or a solution of that substance in carbon disulfide. In 1918, S. J. Peachey, an English rubber chemist, invented the dual gas cold vulcanizing process, in which rubber is vulcanized by being exposed alternately for ten minutes to sulfur dioxide gas and thirty minutes to hydrogen sulfide gas. The gases diffuse into the interior of the rubber and there react to liberate sulfur in a finely subdivided and highly reactive form:



Or solutions of rubber in benzol or naphtha may be separately saturated with the two gases. On mixing the solutions, they set to a transparent gel of fully vulcanized rubber.

Finally, rubber has been cured by sulfides of phosphorus and compounds that do not contain sulfur at all. Chlorides, bromides, phosphides, chlorine gas, sulfurous acid, trinitrobenzene and other nitro compounds have all been successfully used, at least on a laboratory scale.

Delicate fabrics are injured at hot vulcanizing temperatures. Cold vulcanizing processes, on the other hand, are often expensive or slow. This has led to the development of a method for vulcanizing rubber latex, due to Schidrowitz, in England, and first published in 1921. The latex as it comes from the tree is first stabilized by the addition of ammonia. Sulfur, zinc oxide, and vulcanizing accelerators are added, and the mixture is heated below the boiling point, or in autoclaves at about forty pounds steam pressure. The resulting product, which consists of a colloidal suspension of vulcanized rubber in rubber latex serum, bears the trade name Vultex. The suspension

**Vulcanized
Dispersions**

medium contains all the resinous and protein substances present in the original latex, which some authorities claim increase the strength of the finished rubber and render it less sensitive to destruction by heat and light.

To fabricate such products as surgeons' gloves, bathing caps and rubber sheeting from vulcanized rubber dispersions, it is only necessary to dip a porcelain, metal or wooden form into the fluid and let the film dry. Since the dispersion carries more rubber than can be dissolved in the usual rubber solvents, fewer dippings are necessary to build up a film of given thickness. The fire-hazard and health-hazard involved in the use of volatile organic solvents are avoided, and the operations of coagulating the latex with acetic acid and then milling the coagulated rubber to incorporate vulcanizers, accelerators and fillers are entirely eliminated. New applications are in rubber-coated fine fabrics, waterproofed imitation leather, waterproofed plush, and rubberized paper and paperboard, which is very resistant to destruction by folding.

When rubber is dispersed in water the microscopic and submicroscopic particles of rubber acquire negative charges of electricity. On passing an electric current through the liquid the particles move toward the anode, and under proper conditions may be there deposited as a continuous, closely adherent film. This invention was made possible by the research of three different organizations in England and the United States (p. 228). It enables concrete, wood, metal or porcelain to be coated with a thin rubber film to which solid rubber may be vulcanized. This overcomes much of the difficulty previously met in forming an intimate bond between rubber and other materials.

Most of the rubber goods on the market are of rubber blended in a mixing or kneading machine with a great many other materials. Unlimited variations in the formulas used in compounding are possible, according to the multitude of

Electroplated Rubber

Rubber Compounding

uses to which the product is to be put. Raw rubber, in the form of smoked sheets, may be mixed with reclaimed rubber, which is usually obtained by treating rubber goods with dilute alkali. Very often so-called mineral rubber is added, which is gilsonite (an inelastic, hard asphaltic pitch of natural origin), mingled with coal tar pitch or the heavy, non-volatile residue from petroleum stills. The strength and wearing properties of rubber are increased by a proper addition of such material. Or the mixture may include factice, which is rubbery material made by treating oxidizable oils with oxygen or nitric acid and sulfur or sulfur monochloride.

To the preceding primary ingredients of the rubber compound may be added softeners, such as pine tar, which make it easier to mix or knead the materials in the rubber mill, or make the rubber adhere better to fibrous materials. Fillers and extenders, such as carbon black, zinc oxide, or light magnesium carbonate may be added. These give added tensile strength and greatly increased wearing qualities to the rubber if added in proper quality and amount, though their original purpose was merely to reduce the cost per pound.

In addition, the rubber compound usually contains a small amount of some substance capable of hastening or accelerating the vulcanizing process, and usually an anti-oxidant. Colored pigments or dyes may be added, or paraffin, which in small amounts affords some protection against the deterioration of rubber in sunlight, and substances designed to accomplish still other results.

Goodyear used white lead (basic lead carbonate) as an accelerator or quickener for the vulcanizing process.

Afterwards litharge (yellow lead oxide) was used, in quantities of five to fifteen per cent of the weight of the finished stock.

Then, in 1906, the first organic accelerator was discovered. This was aniline, $C_6H_5NH_2$. It was followed by a great many others, mostly compounds of nitrogen.

**Vulcanizing
Accelerators**

Some of the most powerful of these accelerators are derivatives of guanidine, $\text{NH}=\text{C}(\text{NH}_2)_2$. A tenth of 1 per cent of a powerful accelerator will cure rubber within five minutes at ten pounds steam pressure or within a few hours at room temperature.

Though the manner of action of the vulcanizing accelerators is not definitely known, it is presumed that they act by combining momentarily with sulfur, then handing this on to the rubber in a finely divided, active condition. Although but a fraction of a per cent of accelerator is incorporated with the sulfur-rubber mixture, the total consumption of accelerators amounts to several thousand tons a year, and their production is an important organic industry.

The deterioration of rubber from ageing is very largely, but not entirely, due to a slow process of oxidation. That a loss of strength begins as soon as the rubber is vulcanized was known as early as 1865, but only since 1924 have any very successful means been discovered for overcoming it. We now know that a great many phenols, primary and secondary amines, amino-phenols and aldehyde-amines have a protective influence, when they are incorporated in vulcanized rubber, in quantities that need not exceed one-half of one per cent. Such substances are known in general as anti-oxidants, though some of them are also vulcanization accelerators as well; indeed some of the earliest known accelerators are fair anti-oxidants. Rubber bands and sheeting which have merely been dipped in a solution of certain anti-oxidants remain perfectly elastic for years.

In addition to loss of strength, rubber also often develops other defects on being aged. One of the most frequent of these is softening, which is due to oxidation or to a reversal of the change that is accomplished by vulcanizing, or to both causes at once. Softening may sometimes be prevented by using an excess of sulfur in the vulcanizing process, together with a vulcanization

Anti-oxidants

accelerator which remains unvolatilized at the temperature of vulcanization. Some anti-oxidants tend to prevent softening.

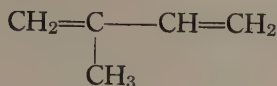
Another defect which rubber may develop on ageing is the so-called tension-cracking, which occurs whenever it remains stretched for a long period, or when it is repeatedly flexed, as happens when boot uppers are folded or when a tire or belt is in use. This defect may sometimes be reduced by the same classes of substances that are known to be effective anti-oxidants. An excellent remedy for tension-cracking has recently been found to be the addition of selenium to the rubber mixture.

The industrial applications of rubber have come about in spite of a comparative lack of knowledge of the chemistry of this substance. Over a hundred industries use products made of rubber, but we are not quite sure of its structural formula. We have learned to make rubber more serviceable by combining it with sulfur, but we do not understand just what the sulfur does to it. We know how to hasten this process by the use of vulcanizing accelerators, but we do not yet know exactly why they act as they do. We protect rubber against oxidation by substances whose protective action we do not understand, and we increase its tensile strength and wearing qualities by adding zinc oxide and lamp black; and then, when the practical art of rubber compounding has been brought to a high degree of perfection, we sit down and wonder how we have accomplished these things. The practical art has outrun science.

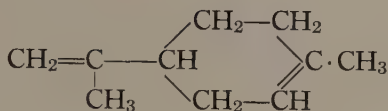
The first clue to the chemical constitution of rubber was obtained by an observation in 1860 that when rubber is strongly heated, out of contact with air, it is decomposed, forming a mixture of liquid hydrocarbons. At least twenty different compounds have since been identified in this mixture, among which isoprene,

**The Practical
Rubber Arts**

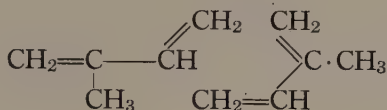
Isoprene



and dipentene,



are by far the most prominent, and form about 30 per cent of the whole. It will be noticed that dipentene may be considered as formed by the direct union of two molecules of isoprene, disposed thus with respect to each other:

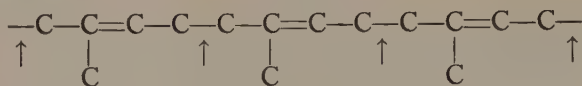


It seemed reasonable to suppose that the rubber molecule itself consists of a complex aggregate of isoprene molecules, linked together in some way. In fact isoprene, on being allowed to stand, is slowly converted into a vulcanizable substance which is very much like rubber. This change can be hastened by hydrochloric acid and a great many catalytic agents. Metallic sodium can cause it to become complete in a few hours.

A great many different structural formulas have been suggested for rubber; but the weight of accumulating evidence, including that published early in 1929, favors that of Staudinger, which represents the rubber molecule as being produced by the direct union of an indefinite number of isoprene molecules, to form a long chain, in which the group $—\text{CH}_2—\text{C}=\text{CH}—\text{CH}_2—$ is indefinitely repeated.



Disregarding hydrogen atoms, such a chain would be represented:



If this view is correct, then when rubber is heated the molecule is broken at the points represented by the arrows, which are those most distant from the double bonds, and the result is isoprene, or a multiple (polymer) of isoprene.

In 1928 it was observed that when rubber is stretched and examined with a beam of X-rays, it shows a pattern that leads to the conclusion that it is composed of parallel strands. Rubber not under tension shows no such pattern. It is suggested that the hydrocarbon chain forming the rubber molecule is in reality coiled like a spring. Perhaps the methyl groups, $-\text{CH}_3$, attached to the chain help to warp or twist it into a spiral. When the rubber is stretched, the coiled molecules are pulled out into parallel straight chains. When the strain is released, they snap back. The "stretch" of rubber, if this is true, is due to the structure of its very molecules. It is significant that no substance not closely related chemically to rubber will stretch to anything like the same degree.

When two molecules of isoprene combine to form dipentene, as pictured on a preceding page, we may think of the ring as being one turn of the original spiral molecule of rubber. When isoprene polymerizes in the presence of sodium, isoprene molecules may link together in the same order as in natural rubber; but some of them may be turned end for end, which will cause the methyl groups, which are attached to the chain, to be irregularly spaced along it. Synthetic rubber made from isoprene is therefore not quite chemically identical with natural rubber. It, moreover, lacks the resinous impurities, which

natural rubber derives from rubber latex, and which may much improve its quality.

The greatly increased life of rubber secured by the use of anti-oxidants, and the constant tendency toward lower

New Uses for Rubber

prices, promise many new uses for this unique material. The most intriguing of these is the production of rubber-coated paving blocks. Bridges and sections of streets in London and elsewhere have been paved with such blocks, with the most satisfactory reduction of noise and vibration. Several different types of blocks have been developed that carry rubber on a base of wood or concrete. Only a lower price for rubber is needed to make rubber-coated streets familiar in our metropolitan centers. Other products made possible by recent improvements in the quality of rubber include rubber joint-rings for concrete pipe, rubberized driving rope for power transmission, rubber sponge for cushions and life preservers, rubber tire-chains, and rubber-coated tile for flooring.

COTTONSEED PRODUCTS

The annual American cotton crop is about 16,000,000 bales or 4,000,000 tons. Cottonstalks, cotton husks and

Cottonseed

seed are produced in vast quantities as by-products. Repeated attempts have been made to use the first two of these as raw material for paper making. As such they are very unpromising. Cottonseed, however, is the basis of a great industry, which the organic chemist serves chiefly in safeguarding the quality of the products and in developing new uses. The operations he controls are typical of those used in working up other oily seeds to produce edible oils or oils suitable for the manufacture of soap, paint and lacquers.

The annual production of cottonseed in the United States is over a million tons. A large part of this is now processed, yielding products worth over \$150,000,000.

The seeds first pass through a cotton gin, which separates the long-fibered cotton, then through a delinting machine, which removes a large part of the short-fibered material, known as cotton linters. This is used as wadding or in the manufacture of felt, or is worked into cloth in admixture with wool, or serves as raw material in the chemical industries that produce rayon, artificial leather, guncotton, dynamite, photographic films, and celluloid.

The delinted cottonseed pass through a machine that cuts them up and removes the hulls. Attached to the hulls are extremely short fibers, which escape being removed by the delinting machine. A process has recently been invented for separating these from the hulls and converting them into paper stock. The hulls themselves may be bleached and seem promising in some of the applications in which wood flour is now used (p. 174).

The seed kernels are now ready to be treated to extract their oil. They are cooked with steam under pressure, until the walls of the cells containing the oil are softened or broken down. The material is then passed through hydraulic presses, which exert a pressure of several thousand pounds per square inch. The oil runs out through the filter press walls and a residue of solid oil cake is left behind.

These operations are all under the control of the chemist. He determines the percentage of oil and moisture in the seed purchased by the mill, and fixes the price to be paid. He must note whether the oil in the press cake has been reduced below the allowable limit, and he must estimate the value of the cake as stock feed, based on the percentage of oil and protein it contains.

The crude cottonseed oil leaving the presses is sold to refiners in tank car lots. It is neutralized with dilute caustic soda, in just sufficient quantities to combine with any free fatty acid that is present. Then it is heated and filtered to

Cottonseed
Milling

Cottonseed
Oil

separate the clear neutral yellow oil from the pasty residue of soap stock. The yellow oil may then be bleached by heating it with a small quantity of an absorbent clay known as fuller's earth. The bleached or unbleached oil is finally deodorized by blowing superheated steam through it for a few minutes.

The refined oil may be hardened into a semi-solid fat by addition of hydrogen (p. 108). Oleomargarine is typically a mixture of oleo oil from beef tallow with neutral oil and hydrogenated cottonseed oil. The product is churned with milk or buttermilk to give it a butter flavor. Lard substitutes generally consist largely of a mixture of hydrogenated vegetable oils, including coconut, cottonseed, corn, and peanut oil.

Cottonseed oil, unhydrogenated, is used as a salad and cooking oil, and for packing olives and sardines. Soaps and cosmetics demand great quantities. Some finds its way into paints and candles. The service of the chemist in the control of the cottonseed industry has resulted in saving and putting to use all of the seed, except often the hulls. Even the untreated hulls are of potential value for the production of furfural (p. 197).

ANIMAL PRODUCTS

The contributions of the chemist in other industries based on the products of plant and animal life are similar to those just outlined for the cottonseed industry. He checks purchased raw materials, controls manufacturing operations, safeguards the quality of finished products, develops uses for by-products, and occasionally modifies the plant or animal material to produce something that is chemically very different. He defends his industry as best he can against the threat of products that may from time to time be produced by chemists who owe allegiance to the opposing camp of the synthetic industries.

His aid in developing uses for by-products is perhaps

the most widely advertised of his services. In the packinghouse industry, no important part of a slaughtered animal is permitted to go to waste. Blood is worked into fertilizer; bone, cartilage and scraps of hide are made to yield glue and gelatin; every stray ounce of fat associated with the viscera is saved for soap stock. Yet such applications of waste materials are often obvious and crude. They have been won by care and system in manufacturing operations and by an alert marketing organization, rather than by chemical research. If cheap transportation and mechanical inventions leading to mass production had existed in the Middle Ages, many of the present practices in the packinghouse industry might readily have been developed without any aid from chemistry.

Yet these operations are all carried on more efficiently because of chemical control; and an occasional product bears witness to the chemist's skill in synthesis or his command of principles that suggest new ways of accomplishing old tasks. Chemistry produced hydrogenated fats, developed methods for the production of improved grades of glue and gelatin, created viscose casings for sausages, and extracted hormones from the glands of animals (Chapter XXIII). On the other hand, chemistry displaced animal glue from some of its former uses by water resistant casein glues; displaced hair by calcium cyanamide as a raw material for the manufacture of cyanides; and threatens to displace the glandular products of animals by their synthetic duplicates. Science does not care whom it serves.

In converting hides into leather, the hides need to be dehaired, swollen, then given a "bating" treatment, designed to dissolve cementing material and expose the structure of interlaced and interlocking fibers. The material is then tanned, which is a chemical change that makes it less readily swollen by water and less readily putrefied by bacteria. Finally, the pores of the leather are filled with a "stuffing grease."

The Packinghouse Industry

Leather

These operations, until recent years, were all carried out by methods inherited from the prehistoric past. The hides were dehaired and swollen with the aid of lime, bated with dung, and tanned with an extract of oak galls or bark. This was slow, primitive and inefficient. About 1900, chrome-tanning was introduced, in which chromium salts were substituted for plant extracts in tanning. The process was thereby shortened from weeks to a few hours. Unfortunately, chrome-tanned leather is inferior in some respects, such as its tendency to swell or shrink with slight changes in its content of moisture. Nevertheless, perhaps three-fourths of the upper leather and a large part of the sole-leather manufactured in the United States and Great Britain are now made by this process.

Since 1920, noteworthy improvements have been made in other tanning processes. Practically useful synthetic tannins will doubtless ultimately be produced, though previous efforts in this direction have been rather disappointing. Very recently it has been shown that a careful control of the degree of acidity of the tan liquor may very much reduce the time required for the tanning process. Leather may now be oak-tanned in a small fraction of the time needed a few years ago.

A spectacular improvement over the disgusting and unsanitary methods of the past has been accomplished by the introduction of bating solutions containing digestive enzymes prepared from the pancreas of animals. These have been widely used as a means for laying bare the fibrous foundation of the hide material, previous to the tanning process proper. Leather substitutes, compounded with rubber, have constantly been improved.

The soap industry uses both plant and animal fats. By being heated with alkalis, fats are resolved into glycerol and the sodium salts of fatty acids, such as sodium oleate, $C_{17}H_{33}COONa$. The chemist in control of soap-making checks the quality of raw materials and finished products and has developed uses for glycerol. Very recently, it has been determined

Soap

which particular fatty acids form alkali salts that are most valuable as soaps. Sodium oleate, for example, is a good soap, but sodium stearate a very poor one. Chemistry has also made some contributions to our understanding of what happens in the cleansing of fabrics by soaps.

Yet the operations of making soap, separating it from liquor and impurities and recovering glycerol have been in charge of men who depended on practical experience rather than on chemical principles. It was the technique of the Middle Ages, perfected by close attention to details, and applied to production on a large scale with the aid of engineering. Only recently has chemical research furnished sufficiently intimate information concerning the soap-boiling operation to put science in control of this ancient art. The most important soap manufacturers employ research staffs that are devoted to a large degree to the scientific study of established methods of production. Science is making a valiant attempt to catch up with practice. A vantage point is just being attained that should permit the development of other methods of soap-making than the ancient process of boiling with alkalis. The famous Twitchell process, which uses steam, in the presence of a catalyzer, is typical of the methods that may be brought into use by a more complete knowledge of chemistry of fats, soaps and the soap-making process.

And now chemistry contributes soaps that are not fatty acid salts at all. Triethanol amine, $(\text{HOC}_2\text{H}_4)_3\text{N}$, is one example from among many groups of synthetic substances which have been found to possess the properties of soaps. The soap industry, like many another, lives under the shadow of coming synthetic substitutes for commodities that are directly derived from plants and animals.

WOOD DISTILLATION

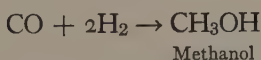
The wood distillation industry affords our final example of the services of the chemist in control. As a means for

producing charcoal it is prehistoric. In early historical times great areas had already been deforested by the producers of charcoal, which was in demand for the production of iron from iron ore and quicklime from limestone. Chemistry first directed attention to useful volatile products that escaped from the top of the charcoal ovens and went to waste. These consisted of combustible gases, together with creosote, acetic acid (pyroligneous acid) and methanol (wood alcohol). Acetic acid was converted into calcium acetate, which on being strongly heated produced acetone.

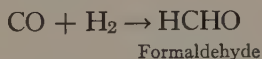
For a long time, wood distillation furnished most of the acetic acid, methanol and acetone used in industry. Then, about 1920, synthetic methanol appeared in the world's markets. Acetic acid, meanwhile, was being synthesized from acetylene and was being produced by the acetic acid fermentation of alcohol at constantly lowered prices. Acetone, too, was being produced by fermentation (p. 268), and even the market for charcoal for the manufacture of crucible steel was being diminished by the increasing use of electric steel. The times were suddenly out of joint for the wood distillation industry.

In the production of synthetic methanol, a mixture of hydrogen and carbon monoxide, at about 400° C., is passed over a catalyzer, which usually consists of zinc oxide and finely divided (reduced) copper.

Synthetic
Methanol

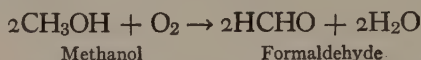


The same reactants, in different proportions and under somewhat different conditions, yield formaldehyde.



The production of synthetic methanol is increasing very rapidly. In 1929 about half of the 9,000,000 gallons

used in the United States was synthetic. About three-fourths of the total use was fairly equally divided between the denaturing of grain alcohol and the production of formaldehyde, which is very readily made by passing a mixture of methanol vapor and air over a catalyzer of reduced copper.



In the emergency produced by the sudden appearance of synthetic duplicates of its chief by-products, the wood distillation industry turned to chemical and engineering research. In the largest recent enterprise felled trees are worked into lumber, and only waste wood and limbs are distilled. Each oven is heated by combustible gases produced by a neighboring oven. When the reaction once begins it is self-propelling, liberating enough heat to maintain the oven temperature without the use of fuel. The continued existence of wood distillation in the face of the competition of synthetic products has been greatly aided by the suddenly increased demand for acetic acid for the manufacture of lacquer solvents, and the demand for cellulose acetate for acetate rayon and non-inflammable film. Yet research contributed economies to destructive distillation without which it must presently have been driven out of existence. The best protection against the research of one's competitors is a program of counter-research.

There are of course many other organic industries under the control of the chemist. Turpentine and rosin are extracted from coniferous woods. Starch, glucose and dextrin are produced from corn, in addition to fermentation products to be described in a later chapter. Sugar is crystallized from the juices of the sugar cane and sugar beet, then chemically refined. Pectin is extracted from apples. Waste citrus fruit is worked over for citric acid and lemon

Other
Industries

oil. Cocoa, spices, vanilla, essential oils of many varieties, linseed oil, drugs, natural tannins and perfumes are all extracted from plants by processes that benefit from chemical control.

Chemical enthusiasts have sometimes claimed all these as chemical arts. The truth is that they were of great importance before there was any science of chemistry, and have but recently learned to make use of chemistry, first in control, then in some slight modification of the natural materials. Many of them are constantly endangered by synthetic products that are perhaps better suited for our purposes than any furnished by Nature.

CHAPTER XVI

GIANTS ASTRIDE THE EARTH

THE organic chemical industries are interrelated in a way that makes it possible for a given development to spread in ever widening circles into the remotest regions of synthesis. A company may begin by producing alcohol from molasses by fermentation. Having made alcohol, it may combine this with acids to form esters for use as solvents in the preparation of lacquers. Thus it may presently manufacture lacquers; or it may convert its alcohol into ethylene to be marketed for anesthesia or the artificial ripening of citrus fruits, or into ether. The ethylene in its turn may be converted into glycol, for use in automobile radiators, or into glycol esters, which are lacquer solvents. Again, an interest in lacquers may lead the company to produce cellulose nitrate or cellulose acetate plastics; or it may convert alcohol into acetic acid and chloracetic acid, and so at length may be engaged in the production of synthetic indigo, in which chloracetic acid serves as a raw material.

The chemical industries thus lend themselves to vertical combinations, in which a given industry absorbs another that furnishes it with raw materials or that uses its products. It is fortunate that this is so, since the products of chemical industry are subject to sudden and violent fluctuations in demand, due to the frequency with which chemical research produces new methods for accomplishing old tasks and new substances that prove superior to those previously used to satisfy the demands of industry. Only a corporation with diversified activities, a wide-

spread marketing organization, and an active research staff, in intimate touch with several different industries at once, can hope to avoid the crises that the swift pace of progress brings to weaker organizations. Great chemical trusts have come into being, in the principal industrial countries of the world. To illustrate how far this process has gone during recent years, let us now pass in review some of the most important of the chemical giants of today, beginning with those of the United States.

E. I. du Pont de Nemours and Company, incorporated in 1915, is a development of chemical activities that began with a small powder mill, established by one of the du Ponts near Wilmington, Delaware, in 1802. This great corporation has employed as many as 1200 research chemists at a single time; and has expended over \$3,000,000 in research in a single year. It owns about 23 per cent of the entire common stock of General Motors, which uses enormous quantities of du Pont products, and which has developed lead tetra-ethyl as an anti-knock ingredient for gasoline (p. 140).

In 1924 the du Pont Corporation absorbed the General Explosives Company, and in 1928 the Grasselli Chemical Company, manufacturers of general chemicals. It operates about twenty explosive plants in widely separated parts of the United States, and has important subsidiary companies, engaged in the manufacture of explosives in Mexico, Chile, and Canada. Its productive capacity, at the close of the World War, was over 200,000 tons of smokeless powder a year.

The du Pont Corporation manufactures a large part of the dyestuffs used in this country, and owns subsidiary companies operating two large rayon plants (The du Pont Rayon Company), two plants for the production of nitrocellulose plastics (The du Pont Viscoid Corporation), and other plants for the production of paints, varnishes, lacquers, Cellophane, and ethyl alcohol. Its

recent process for the production of glycerol by fermentation (p. 268) is intended to supply its own explosive plants with the raw material for nitroglycerine, an ingredient of dynamite. It produces methanol by hydrogenation (p. 219) and owns most of the stock of the du Pont Ammonia Corporation, which came into being in 1929 to produce synthetic ammonia. The du Pont Corporation has plants for the production of wood flour, for the manufacture of dynamite and plastics, and others for the production of purified wood pulp for the manufacture of paper and cellulose products.

The Allied Chemical and Dye Corporation was created in 1920 by the consolidation of the General Chemical Company, manufacturers of heavy chemicals; the Solvay Process Company, producers of sodium carbonate, caustic alkalies, and chlorine; the Semet-Solvay Company, producers of coke, coal tar and other by-products of the coke oven; the Barrett Company, producers of coal tar products, including roofing material and road-making material; and the National Aniline and Chemical Company, manufacturers of dyestuffs. It subsequently acquired the Atmospheric Nitrogen Corporation. This operates a nitrogen fixation plant at Syracuse, N. Y., and in 1928 began to operate the first unit of a new plant at Hopewell, Va., which will produce 90,000 tons of fixed nitrogen a year, and is stated to have cost \$35,000,000. Other plants are to follow.

This corporation is an excellent illustration of the manner in which chemical companies expand by extending their activities into industries that begin where the primary activities of the original group leave off. In the processing of coal, the chief products are coke, gas, ammonia, creosote, and tar. The group exploits the first two of these in the field of metallurgy. It combines ammonia with sulfuric acid, for the production of ammonium sulfate fertilizer and delivers ammonia to plants produc-

ing sodium carbonate by the ammonia or Solvay process. It produces benzene, toluene, anthracene, and phenol from coal tar, and uses these in the manufacture of dyes, phenolic resins, and lacquers. It develops tar composition roofings and road materials, and rubber compounds containing tar. It controls the United States Rubber Company.

The Allied Chemical and Dye Corporation is remarkable for its financial strength. At the end of 1928 it distributed nearly \$16,000,000 in dividends and had left over a surplus of more than \$11,000,000, which it added to a previous surplus to make a total capital and profit surplus, accumulated during nine years, of nearly \$182,000,000.

The Union Carbide and Carbon Corporation was incorporated in 1927. It is a development from a small company which acquired the Willson carbide patents, in 1892. It owns all the common stock of over 35 subsidiary companies, which are pioneers in their respective industries. These subsidiaries, in 1929, had 145 plants in continuous operation. They maintain large laboratories for fundamental scientific research, which have developed many products and processes that are entirely new to industry.

The subsidiary companies, in the United States, Canada and Norway, produce cobalt, silicon, chromium and manganese alloys. They are the largest manufacturers of ferro-alloys, such as ferro-chromium, ferro-manganese, ferro-silicon, ferro-tungsten and ferro-vanadium. These are of importance in producing special steels, which are used in quantity in modern industry.

Other subsidiaries produce a great variety of carbon products, including electrodes for electric furnaces and arc lamps and brushes for electrical generators and motors. They have extended their activities into the industries that use electrode carbon, and now produce dry cells, for flashlights and radio sets. In 1928 the Acheson

Union
Carbide

Graphite Corporation was acquired, which produces most of the artificial graphite made in the United States.

In the organic chemical field, subsidiaries manufacture and sell calcium carbide and acetylene and apparatus for their utilization. Important organic chemicals thus far produced by this company include ethylene dichloride, acetone, ethylene glycol, diethylene glycol, and those bearing the trade names Cellosolve and Methyl Cellosolve (p. 142).

Because acetylene must be used in conjunction with oxygen, a subsidiary produces oxygen on a vast scale from liquid air. Nitrogen and the rare atmospheric gases are obtained as by-products of this process. Propane and other hydrocarbon gases are also produced and marketed in cylinders as portable fuel for cutting metals and for industrial and domestic use.

The Dow Chemical Company of Michigan manufactures caustic soda, chlorine and other inorganic chemicals.

**The Dow
Chemical
Company** It produces a large part of the world's supply of bromine. It is actively interested in the development and manufacture of magnesium and magnesium alloys for airplanes and dirigibles. It produces a number of organic chemicals, chiefly those containing bromine or those in the synthesis of which chlorine or bromine is required.

A recent accomplishment of the Dow Company is the development of a cheap method for the synthesis of diphenyl oxide. This is a solid, white when pure, which melts at 27° C. Alone, or in admixture with a related substance, diphenyl, it has been brought forward as a substitute for steam in the vacuum distillation of lubricating oils and as the high-temperature fluid in a two-fluid power plant. Added economy as compared with steam is found in the fact that high temperatures may be reached, at which steam displays inconveniently high pressures.

The Standard Oil Company of New Jersey is not only

the world's leading producer of petroleum, but a great chemical corporation. It is the second largest producer of natural gas, which has recently become a promising source of raw material for chemical synthesis (p. 135). It has entered into an agreement with the I. G. (German Chemical Trust) that permits it to make use of the processes that the latter has developed for the production of gasoline by the hydrogenation of petroleum still residues and heavy crudes. A plant now building at Bayway, N. J., will have a capacity of about 5000 barrels a day by this process, in 1931. Similar plants are under construction at Baton Rouge, La., and Baytown, Texas.

Standard Oil International Combustion Engineering Corporation was incorporated in 1920. It is a great holding corporation, controlling subsidiaries engaged in the refining of coal tar and the manufacture of a wide range of products produced from coal tar. Much of the tar used in these refining operations is produced by subsidiaries which operate plants for the low-temperature carbonization of coal. Other subsidiaries are engaged in the design, manufacture and installation of fuel-burning and steam-generating equipment (stokers, pulverized fuel equipment, boilers of all types). The operations of this organization are carried on by subsidiaries in the United States, Canada, Europe, Asia, South America, Africa and Australia.

International Combustion Engineering Corporation The Air Reduction Co., Inc., was incorporated in 1925. It is one of the foremost producers in this country of oxygen, nitrogen, argon, neon, helium, krypton and xenon from liquid air; also liquid oxygen, nitrogen and air for the production of low-temperatures; and calcium carbide and compressed dissolved acetylene. It has entered the field of oxyacetylene welding, and has developed several types of manual and automatic oxyacetylene

Air Reduction Company

cutting and welding apparatus and machines, and is extending its activities into the production of organic chemicals. It recently acquired a large interest in the United States Industrial Alcohol Co., which, itself, is a consolidation of several of the largest producers of fermentation alcohol.

The Eastman Kodak Company, best known for its cameras and photographic equipment, is the world's leading producer of photographic chemicals and film. Its production of photographic film amounts to more than a billion feet a year. Its main plant at Rochester, N. Y., has 400 acres of ground and more than seventy buildings. It has recently erected a large plant at Kingsport, Tenn., for the production of acetic acid by destructive distillation of wood waste (p. 220). It has begun the manufacture of non-inflammable cellulose acetate film. Jointly with the Anode Rubber Company, Limited, of Great Britain, and the Goodrich Rubber Company, it controls the process for the production of rubber specialties by electro-deposition from rubber latex (p. 207).

In the United States the amalgamation of chemical industries is hindered by the Sherman Law. Such combinations as have been effected have rather been made by the association of industries that are so related that the product of one becomes the raw material of another. In Europe, similar legal restrictions, tending to prevent the amalgamation of competitors, do not exist.

In 1926 a gigantic merger of British chemical corporations, known as Imperial Chemical Industries, Limited, came into existence by the amalgamation of Brunner, Mond and Company, Ltd.; Nobel Industries, Ltd.; British Dyes, Ltd.; and the United Alkali Company, Ltd. These were themselves the result of previous consolidations, which have now brought a total of 75 constituent and associated companies under one direction.

Imperial Chemical Industries is the largest industrial corporation in the British Empire. Its extended marketing organization carries its products to all the Colonies and Dominions. It has recently employed about 53,000 men, and produces products amounting to millions of tons each year, with a value of scores of millions of pounds. It operates great acid, alkali, rayon and explosive plants, mines and quarries millions of tons of coal and limestone each year, and smelts great quantities of ores, for the production of non-ferrous alloys. It has an enormous production of calcium cyanamide, synthetic ammonia and a diversified line of nitrocellulose products, lacquers, paints and organic chemicals. It manufactures more than five thousand different dyestuffs and intermediates, amounting in 1928 to over 25,000 tons.

Germany is the place of origin of the cartel, an association of producers to regulate production, fix prices and pool sales. The German chemical industry, at the close of the war, found itself over-developed, and the cartel was the most logical means of escaping the disaster of uncontrolled competition. Indeed, the German potash cartel is created by law and exempted from decisions of the Cartel Court, which was brought into being to correct certain abuses of the system.

**The German
Dyestuff
Cartel**

The dyestuff cartel has been brought about by a number of associations, the earliest dating back to 1905. In 1925 a complete merger of all the principal organic chemical corporations of Germany was made, with a paid-up capital of about \$250,000,000. This huge trust, commonly known as the I. G. (Interessen Gemeinschaft der Farbenindustrie) links together over a hundred chemical manufacturing corporations, factories and mines, with more than a score of selling companies in foreign fields. Its marketing organization covers the whole world.

The I. G. owns numerous lignite mines, blast furnaces, and factories for the production of inorganic chemicals of

all sorts. It is actively furthering the use of magnesium alloys. In the organic field it controls
Activities of the I. G. nearly all the German dyestuff production, which now supplies about 25 per cent of the world's markets. It operates several great rayon and cellophane factories, manufactures calcium carbide and its numerous derivatives on a grand scale, processes millions of tons of coal for the production of coke and by-products, and is actively furthering the development of the Bergius process for converting coal into liquid fuels by the action of hydrogen under pressure (p. 160). In 1928 it produced about 50,000 tons of gasoline by this process, from lignite. The process should produce about 250,000 tons of gasoline in 1930, and will probably soon supply a large part of Germany's needs for motor fuel. For this development the I. G. is especially well fitted by reason of its great reserves of coal and lignite, the supplies of hydrogen produced as a by-product of its activities in the inorganic field, and its far-flung marketing organization. It recently acquired 40 per cent of the capital stock of the Ford Motor Company of Germany.

The I. G. was the first to produce synthetic methanol (p. 219) on a large scale. It is the world's most important producer of fixed nitrogen by the cyanamide and other processes and supplies about a third of the world's needs for fixed nitrogen. It has entered the mixed fertilizer field in alliance with the German and Alsatian potash trusts. It has important interests in the manufacture of synthetic perfumes, medicines, photographic chemicals and films, linoleum, vulcanized fiber, explosives, lacquers, synthetic camphor and synthetic resins. It threatens to appear any day in the markets of the world with synthetic rubber. In 1928 it employed 108,000 persons, not including those in its mines. Its total exports to countries outside of Germany, in recent years, have been over \$150,000,000 annually.

In 1929 the great Leuna Works of the I. G., at Oppau-

Merseburg, combined about 600,000 tons of nitrogen, obtained from liquid air, with hydrogen obtained by the action of steam and air on coal, to form ammonia by the Haber-Bosch process. This is a direct union of hydrogen and nitrogen gases under pressure. In addition, the I. G. fixed 80,000 tons of nitrogen in the form of calcium cyanamide, during 1929. Its total present productive capacity of fixed nitrogen is 770,000 tons. This may be compared with the American annual demand of about 500,000 tons of combined nitrogen, of which about three-fourths is for agricultural use as fertilizer. The production of fixed nitrogen in the United States, in seven plants operated in 1929 was only 84,000 tons.

The interconnections of the I. G. with chemical corporations outside of Germany are impressive. It holds certain properties jointly with the Nobel Industries of Great Britain. It shares other interests with British, Belgian, Swiss, Spanish, and Italian rayon, celanese and dyestuff corporations. It supports and partly owns Norsk-Hydro, which is engaged in the production of nitric acid and nitrates from the nitrogen of the atmosphere by the electric arc process. It is extending its operations into the nitrate fields of Chile. In the United States it has recently organized the American I. G. Chemical Corporation, for the acquisition of certain American chemical companies, including interests in the Agfa-Ansco Corporation and the General Aniline Works, formerly the Grasselli Dyestuff Corporation.

In France, the amalgamation of the principal organic chemical corporations into a single trust or cartel was accomplished in 1928. At that time the forty companies existing in 1914 had been reduced by combination and elimination to four. The leader of these is the Kuhlmann Corporation, which began as a sulfuric acid factory in 1825, and now

*Ammonia
from
Liquid Air*

*Joint
Interests*

*French
Companies*

produces a great variety of explosives, dyestuffs, rayon, and other organic products, corresponding to the products of the du Pont Corporation, in the United States. In 1927 it produced 446,000 tons of superphosphate fertilizer, 500,000 tons of chemicals and 8,000 tons of dyes.

The other partners in the French chemical trust are St. Gobain, which is the chief producer of acids, alkalies, glass, fertilizers, and heavy chemicals; "Pechinoy," which dominates the electro-chemical industries of France; and the Nitrogenous and Composite Fertilizer Company, which produces fixed nitrogen products on a large scale. These companies have recently greatly increased their working capital, and have an enormous extension, not only in the dyestuff industry but in the production of cyanamide, rayon, pyroxylin plastics and lacquers.

Before the World War France imported nearly 90 per cent of her dyestuff needs, chiefly from Germany. At present she produces 95 per cent of her own needs and exports considerable quantities of dyestuffs. The manufacture of rayon has increased by leaps and bounds. The Kuhlmann Company controls twelve other French concerns, representing a great variety of organic products of all sorts, including 70 per cent of the French dyestuff production. Association between manufacturers of rayon and units in the textile industry are being made. Both the Kuhlmann Company and the I. G. possess large holdings in the Swiss dye companies.

Montecatini, Società Generale per l'Industria Mineraria ed Agricola, was founded in 1888. It is a great holding corporation, bearing the same relation to Italy that Imperial Chemical Industries does to the British Empire. Its inorganic products are sulfuric and nitric acids, copper sulfate, aluminum, synthetic ammonia and mixed fertilizers. Organic products include explosives, nitrocellulose plastics, rayon and solvents. It operates numerous mines and quarries and uses about one-tenth the total electrical en-

ergy produced for light and power in the Kingdom of Italy.

The relative sizes of the great chemical corporations of the world may be roughly estimated from the following approximate figures, expressed in millions of dollars.

**Comparative
Statistics**

	Net Profits after Depreciation 1928	Paid in Dividends 1928
Standard Oil of New Jersey.....	134	36.6
du Pont Corporation.....	64	49.7
I. G.	28	27
Allied Chemical and Dye.....	30	15.8
Union Carbide and Carbon.....	30.6	16.2
Imperial Chemical Industries.....	26.0	20.0
Eastman Kodak.....	20.0	16.8
Montecatini	5.0	4.8
Air Reduction.....	3.5	2.0

In 1928 an international cartel came into being. The great German Dye Trust concluded a working agreement with the French Dye Trust and the leading Swiss producers of dyes, for the exploitation of foreign markets, giving a definite fraction of the total exports of the group to each of its members. The two most bitter opponents in the World War have come to an economic understanding. The total value of dyes exported by the combination, in 1928, was nearly \$94,000,000.

There is little doubt that an agreement will eventually be reached between the French and German trusts, on the one hand, and Imperial Chemical Industries, Ltd., of Great Britain, on the other, on account of the great surplus that exists of dyestuff production capacity as compared with actual production, in all the principal countries of the world.

**International
Dye Cartel**

	Dyestuff Capacity (tons)	Actual Production (tons)
Germany	200,000	20,000
United States.....	57,000	44,000
Great Britain.....	40,000	17,000
France	22,000	16,000
Switzerland	16,000	11,000

Combinations and agreements still continue to be made. Economy in selling and mutual financial support are not the only purposes of union. By the pooling of information and research processes and by the exchange of patents a great advantage is obtained by all who participate. Discoveries by one member become available to all, and promptly benefit industries that seem to be but distantly related to the one responsible for them.

The I. G., for example, cooperates with the Standard Oil Company of New Jersey in the production of synthetic motor fuel; with the du Pont Corporation and with the Nobel Industries, Limited, of Great Britain in the manufacture of explosives; with the Dutch Shell; with Courtaulds (the largest British producer of rayon); with Enka (leading Dutch producer of rayon); with Montecatini, in Italy, for the licensing of patent rights for the production of mixed phosphorus-nitrogen fertilizers; and with Petschek, a banking group controlling lignite mines in Czecho-Slovakia.

Similarly, L'Air Liquide, a branch of Kuhlmann, in France, cooperates with the German potash syndicate in the marketing of mixed fertilizers, and has an arrangement with the du Pont Corporation for the production of synthetic ammonia by the Claude process, which was developed in France. It seems very likely that the production of fixed nitrogen by this process and other processes may presently become so great as to lead to the estab-

lishment of an international cartel for the marketing of nitrogenous fertilizers.

Indeed, the agreements that are reached with regard to mutual support in research and development all tend at length to include provisions for the division of markets. The whole world seems tending toward a great consolidation which will control the production and distribution of most of the world's supply of fixed nitrogen, synthetic fuels, and organic chemicals. This means a control of the world's food, transportation, and a multitude of material comforts. The whole world will pay tribute to such a consolidation. Let us hope that the consolidation may prove to be a powerful influence in maintaining the peace of the world.

Thus ends our story of how the foundations of the science of organic chemistry were laid, and what has come of it down to the present hour. New materials have been brought into being which the world never knew before. Old materials have been put to new uses, and have been applied more effectively than ever before, because of our new understanding of their inner nature. Our very speech has been altered by the coinage of new words that record the swift pace of chemical progress: Pyroxylin, rayon, Celanese, Bakelite, Cellophane, methanol, cyanamide—familiar commodities these, though their very names were unknown a few years ago.

New enterprises have been set afoot in all the fields of commerce. New industries have sprung up. Coal tar discards its black mantle and assumes the garments of the rainbow. Wheels whirl in great factories condensing the air we breathe into liquid form, at the rate of a million tons a year, for the manufacture of fertilizers and high explosives. Coal veins are struck with the staff of chemistry, and liquid fuels gush forth. The voices in the market place speak familiarly of catalytic processes,

nitrogen fixation, vat dyes and synthetic ammonia. Nation lends aid to nation in developing the resources of the globe for the comfort and well-being of humanity. Former enemies join hands across vanishing frontiers. Giants spring from the earth and cast their shadows over continents.

The wonders in the midst of which we move give promise of greater wonders yet to come. The synthetic chemist is credited with unlimited powers. We are apt to forget that the chemical compounds that compose our food are furnished us, ready made, by living plants and animals. Rayon is something new, but it is still cellulose, the outstanding product of plant life. Petroleum, coal and natural gas, with all their chemical possibilities, are derived from life that flourished on the earth in prehistoric ages. The synthetic skill of Man is not yet independent of the synthetic skill of Nature.

Has his skill surpassed that of Nature? In answer, let us see what sorts of chemical transformations are accomplished and what sorts of chemical syntheses are induced by the inhabitants of the living universe of bacteria, plants and animals.

PART III

THE CHEMICAL ACTIVITIES OF LIVING
CELLS

CHAPTER XVII

MICROSCOPIC LIFE

LIVING things have some characteristics that place them in contrast to the non-living. They grow by a rhythmic process in which cells divide and redivide — something quite different from the straightforward, steady growth of a crystal. They react in a very complicated way to impulses that reach them from without, and they adapt themselves to changing conditions by changing their forms and structures. They reproduce, and thus maintain themselves as a race, though they perish individually.

The biophysicist and biochemist study the transformations of energy and matter that take place in the processes of life. The sorts of energy they encounter are those familiar in the inanimate world. The elements they meet are a dozen or so of those most common in air, water and soil. The classes of compounds they recognize have frequently been synthesized in test-tubes and beakers, without the aid of living beings.

Is life, then, merely the result of ordinary forces, energies and materials, interwoven with a complexity quite unknown in the inanimate world? It seems very possible. It is the professional duty of the biochemist or biophysicist to see how far the laws of the non-living extend into the realm of the living. The thoughtful reader will understand that life is not less wonderful or worth while, nor its spiritual possibilities less real, because of our increasing knowledge of its dependence on the ordinary laws of matter and energy.

The simplest living things consist of single cells, of microscopic size, or even large enough to be seen with the naked eye. Organisms that are a little more complex form clusters, chains or branching groups of cells. In the higher plants and animals, cells of different sorts and shapes are assigned different duties and may be assembled in groups to form special organs. The body of a man contains several billion cells, of many different shapes and kinds, adapted to the most diverse purposes.

Living cells are filled with a complicated mixture of fluid or gelatinous material, called *protoplasm*. This is a protein *sol* (a fluid colloidal dispersion) or *gel* (a jelly), in which are dissolved salts, suspended droplets of oily liquid and granules of different sorts of semi-solid materials. These various parts of the contents of a cell differ in their chemical natures, one from another, and serve different ends. Even in simple, one-celled organisms they are often built into characteristic structures. A single living cell is like a factory or office building, having different parts devoted to the most varied occupations. Moreover, the chemical nature of the contents of a cell is different in different species and even in individuals of the same species, and depends upon the part that the cell as a whole must play in the life of the organism.

Protoplasm is as diversified as the animate universe, for within it is hidden all the marvelous mechanism of heredity. In the germ cells the microscope can distinguish minute structures called *chromosomes*, which hand on the characteristics of the race, from parent to offspring, to the most remote generations. It is the chromosomes that determine whether a germ cell is to develop into a mushroom or a pine tree, a mouse or an elephant, a blacksmith or a prima donna. There is a definite number of chromosomes in the germ cells of each species—forty-eight in the case of man—and these must carry all the infinitely varied characteristics of

the individual. Somewhere in the chromosomes of your parents there lurked molecules of a chemical configuration that determined whether you were to have blue eyes or brown, capacity for mathematics or music, resistance or lack of resistance to communicable diseases, a masterful and purposeful life or an existence chiefly devoted to eating food and wearing out clothes.

The marvel is that some of the ingredients of protoplasm must be so extremely alterable as to permit the organism to respond to a beam of light, a breath of air or the faintest suggestion of acidity; whereas others determine a physical form and physiological activities that gradually alter from generation to generation, in the slow course of evolution; and still others determine characteristics that remain unchanged while mountains are worn away and the ocean bottoms are uplifted into dry land, during the lapse of ages. Many simple organisms that occur in fossil strata laid down millions of years ago are indistinguishable from forms that flourish on the earth today. Some eternal principle has stretched like a guiding hand down through all the eons of time, determining that certain types of molecules and certain types of structure shall be duplicated unvaryingly.

All the activities of a living organism, in the last analysis, are chemical activities. Every response to a stimulus, every adaptation to surroundings, every change in form or position is accomplished by chemical changes in the protoplasm.

Sources of Energy

We are complexes of systems in chemical equilibrium. It is through reversible chemical reactions—through adjustments of chemical equilibrium in response to changed conditions—that we live and move and have our being. In growth and reproduction, moreover, every organism needs to build new protoplasm, synthesizing proteins, carbohydrates, fats, phosphatides, pigments, enzymes and a host of other special substances. A single microscopic cell, working smoothly and quietly without fuss or fumes,

may produce dozens of complex compounds never yet synthesized by man.

All these synthetic processes require, not merely a supply of raw materials, but a supply of energy. The most favored organisms are those that may make use of the energy of the sun's rays. These are the green plants. Every green leaf, during every hour that the sun shines, is busily at work, making use of the solar energy in upbuilding starch, cellulose, protein and other complex molecules from the carbon dioxide of the atmosphere and the water and minerals of the soil. We shall examine this process more closely hereafter; but let us pause now to note that it is accomplished with the aid of the green coloring matter called *chlorophyll*, which assists in the reactions in which the green plant absorbs solar energy.

The earliest forms of life upon the earth may have been one-celled, microscopic plants containing chlorophyll. Or they may have been a group of bacteria that contrive to combine synthesis with processes in which energy is released by the oxidation of readily oxidizable inorganic materials, such as hydrogen sulfide and ferrous salts. These so-called *autotrophic*, or self-energizing bacteria, lead the most independent sorts of lives, making themselves at home in situations in which no life has preceded them, and carrying on their synthetic activities at the expense of the energy of their inorganic surroundings, whether the sun shines or not.

These simple one-celled pioneers of life must have had the whole earth to themselves for a very long time. During this period organisms appeared that learned, as some members of human society have learned, to make use of the labors of others. These are the *saprophytes*—the scavengers of the plant world—which derive their energy by oxidizing dead organic matter; and the *parasites*, which attack or engulf the living.

No one really knows whether one-celled green plants or autotrophic bacteria were the first to take possession

of our planet, nor how the complex organic molecules came into being that must have been needed to bring about the earliest and most simple manifestations of life. The most primitive forms of life perhaps had fewer and simpler chemical activities than any organisms now known. They perhaps operated under the stimulus of simple inorganic catalyzers, and only gradually assumed new activities. We might have the clue to the origin of life itself if we knew more about enzymes (p. 263), for these are able to set complicated reactions in motion that would otherwise not take place. We do not make the origin of life less mysterious by presuming, as some have done, that life first reached the earth from some distant part of space, in the form of bacterial spores. Life, for all we know, may have existed and may be destined to exist from eternity to eternity, along with matter and energy.

As time went by, the primitive forms of life developed new complexities of form and function and engaged in new chemical activities. The one-celled pioneers of life then had to share the earth with masterful many-celled new arrivals, including simple animal life. Animals are all parasites, really, for they all derive their energy by oxidizing materials that have been built up by plants or by other animals.

Yet still, as ages passed by, the capacity of protoplasm for assuming new complexities and new responsibilities produced new forms to lend a hand in the age-old game of building up and tearing down: molluscs, insects, fishes, reptiles, birds and mammals. Finally, among the most recent forms of mammals appeared one which we, in our more optimistic moments, regard as a masterpiece of creation—Man. Protoplasm was now entering gropingly into the chemical activities that are incident to *thought*. Yet evolution still unfolds. The future will see the earth possessed by a race in full command of faculties that have only just begun to dawn in man.

Leeuwenhoek, a Dutch contemporary of Newton and Boyle, produced some of the earliest compound microscopes, after he had developed the art of grinding, polishing and mounting small lenses. These microscopes were capable of magnifying 40 to 160 diameters. With them he set to work with the greatest enthusiasm, examining everything that might prove interesting. He had the whole field to himself. So few observers of the microscopic universe had preceded him that he could not help making startling discoveries whichever way he turned. He described and pictured many different types of micro-organisms, and showed that they are present in our food and drink, and flourish wonderfully in stagnant water, in fermenting fruit juices, in material scraped from the surface of the teeth, and wherever else they are supplied with conditions favorable to their life.

Other microscopists hastened to add their observations, and the suggestion was not long delayed that these swarming "animalcules" might be the cause of communicable diseases, which often spread in such a mysterious way through whole populations. Yet two centuries passed before these suppositions were supported by proofs, and the fact established that the control of communicable diseases merely calls for the control of disease-producing micro-organisms.

Other early observations had to do with fermentation. Since prehistoric times, in all parts of the world, men have prepared alcoholic drinks by permitting fruit juices or starchy grains or tubers to ferment. Another ancient process is that in which dough is caused to rise by adding a little "leaven"—usually a small portion of dough which has already risen. The early Romans must have suspected that these two processes of fermentation had much in common, for they understood how to prepare new leaven from fermenting grapes. Then, when the science of chemistry

Early Observations of Micro-organisms

Fermentation



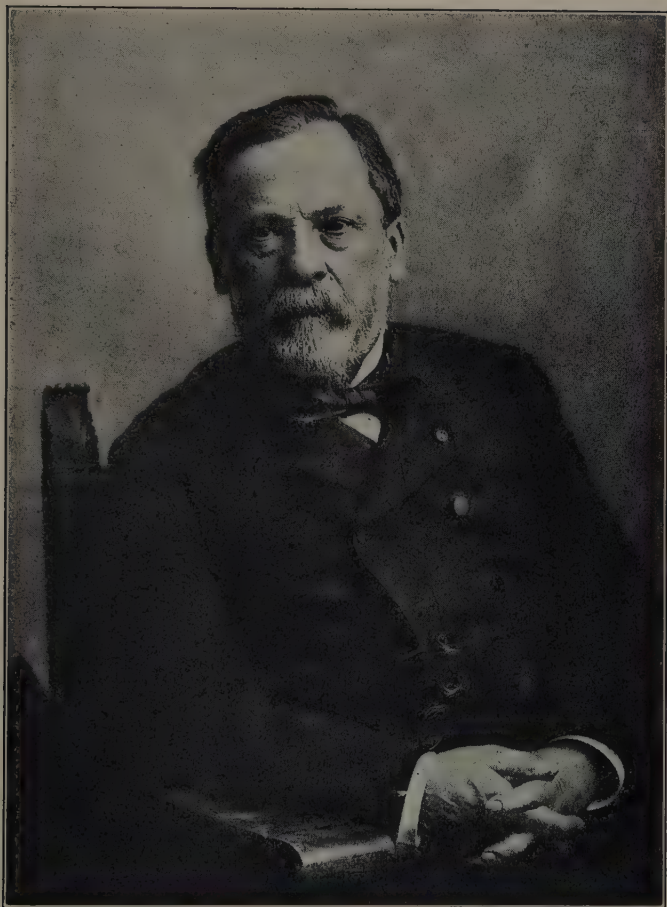
Courtesy of the McGraw-Hill Publishing Co.
LEEUWENHOEK DISCOVERS BACTERIA.

had come into being, it was discovered that both processes produced alcohol and carbon dioxide.

Finally, in 1837, it was proved that fermenting fruit juices and rising dough both contain living cells, of identical appearance, which grow and multiply in these materials. This was the discovery of *yeast*. It was found that yeast taken from either process can be used to initiate the other, and that neither process will take place if yeast is absent. In brief, the fermentation of fruit juices and the rising of dough both consist in the transformation of sugar into alcohol and carbon dioxide, through the action of a definite micro-organism. Yet *how* this micro-organism brings about the chemical transformation that accompanies its growth was destined to remain a mystery for over fifty years more.

In 1850, after microscopic life had been under observation for two whole centuries, the science of bacteriology had hardly made a beginning. Not a single disease had been definitely traced to micro-organisms; and, except for yeast, the chemical changes induced by micro-organisms were completely unstudied. This was the more remarkable when we recall that the science of chemistry was by this time well established, through the work of Boyle, Lavoisier, Dalton, Avogadro, Davy and Faraday. Liebig, Dumas and others had begun the researches that were to lead to the synthesis of thousands on thousands of organic compounds. Yet the world still waited for a master mind to disclose the habits of life and chemical activities of the inhabitants of the microscopic realm.

This was the service of a French scientist, Louis Pasteur, who turned from purely chemical studies, at first regretfully, to investigate some of the problems that were presented by micro-organisms. His first work was to show that fermentation is not always induced by yeast and does not always produce alcohol and carbon dioxide. He found that the active agents in wines that had devel-



Courtesy of Rudolf Lesch

LOUIS PASTEUR

Born at Dôle, 1822. He discovered the methods now used for the separation of racemic mixtures into their optically active components. His investigations in bacteriology continued from 1854 until his death in 1895.

oped unpleasant flavors were not yeast cells at all, but much smaller organisms which we now call *bacteria*. Moreover, each type of bacterium acted on the sugar of the fermenting juice to give a different product, one organism producing acetic acid, another lactic acid, and so forth. The problem of controlling the flavor of wine was thus one of controlling the type of organism which was to grow in it.

Pasteur discovered that by heating the unfermented liquid to a moderate temperature, the undesirable bacteria are destroyed. This is the process of pasteurization, now so commonly applied to milk. About this time also he completed the proofs, which had been accumulating for nearly two hundred years, that life never comes into being save from other life of the same kind. Consequently, when micro-organisms have been destroyed by heating or by other means, the material concerned will remain free from them until they are reintroduced from some outside source.

The success of Pasteur in dealing with the "diseases" of wine led to an appeal for his help in combating pébrine, a disease of silkworms, which was ruining the silk industry of France. Five years of work showed that pébrine was due to a protozoön (p. 251), and that it might be controlled by raising silkworms only from strains which had been shown by microscopic examination to be free from the disease. This directed the attention of the world to a definite disease caused by a definite micro-organism; and though it concerned silkworms, it taught a lesson of sanitation that was later applied to human diseases. Lister, an English surgeon, at once guessed that the pus and gangrene of wounds must be caused by micro-organisms. He took measures to exclude them from wounds produced in surgical operations (p. 156), and thus in a single stroke (1867) ended the misery that had attended the infection of wounds since the beginning of human history.

From this point onward we must interweave the story of Pasteur with that of his great German rival, Robert Koch. France and Germany came near to having equal honors in the progress of the next twenty years (1870-1890). Quite independently, both Koch and Pasteur showed that anthrax, a serious disease of sheep and cattle, was caused by a tiny rod-like organism. For the first time, the organism causing a disease was obtained in pure culture, that is, free from other organisms. After being maintained in pure culture for several generations, in artificial media, the smallest drop-let of it, injected into the blood of a healthy animal, invariably caused the disease. Koch made a thorough study of the form and habits of growth of the organism, and Pasteur showed how the disease might be controlled.

Next, Koch (1880) made a number of improvements in experimental devices: methods for preparing pure cultures, methods for fixing and staining bacteria so that they might be more readily observed and photographed, methods for illuminating objects to be viewed under the microscope, and methods for cultivating bacteria in pure colonies of visible size. These inventions enabled progress to go forward at a rate never before approached. Koch himself immediately discovered the microscopic cause of what is called the great white plague—tuberculosis. Other workers soon afterward discovered the organisms responsible for typhoid, diphtheria, glanders, cholera, tetanus and several dozen other diseases of man or of animals. It is possible that every species of animal is subject to diseases due to microscopic enemies. Some of these attack man, but most of them, very fortunately, do not. Since 1890 progress has been chiefly concerned in elaborating the methods and principles that were developed by Pasteur and Koch. Some of the most serious diseases have been brought under complete control.

Micro-organisms are so called to indicate that most of them are too small to be visible to the unaided eye.

Types of
Micro-organ-
isms

They are also popularly called "microbes" or "germs." As we now recognize them, they are usually classified into five main groups:

1. *Algae*. These are microscopic, one-celled, green or blue plants. They reproduce by dividing crosswise, so that one individual becomes two. By repeating this process, long chains or filaments of cells are sometimes formed. Since the algae are supplied with chlorophyll, or something very like it, they are able to make use of the energy of the sun's rays, after the fashion of the higher plants.

2. *Yeasts*. These are microscopic, one-celled, colorless plants. They usually reproduce by forming small buds, which develop in size, and then either become separated or remain attached to the original cell to form short branching chains. They lack chlorophyll, and must therefore derive their energy by tearing down organic compounds that have been built up by other living organisms.

3. *Fungi*. These grow as a network of fine threads, on which are borne fruiting bodies containing a multitude of minute, rounded reproductive cells, called spores. The fruiting body may be of considerable size, as with mushrooms; but in any case the larger part of the plant is the mass of delicate threads, which spread through the ground or in decaying wood in every direction. They lack chlorophyll, and obtain their energy in the same manner as the yeasts. The simplest forms in each of the several groups of fungi are called *molds*.

4. *Bacteria*. These are much smaller than the yeasts and molds, some probably being even too small to be seen with the microscope. They have the utmost diversity of form. They are devoid of chlorophyll, and are accordingly compelled to obtain their energy in the same manner as the yeasts and molds—at the expense of organic compounds which other living organisms have built up. A

few, however, are parasitic. Conspicuous among these are the bacteria that are responsible for certain plant and animal diseases. Finally, there are a few (autotrophic bacteria) which can derive their energy by the oxidation of inorganic material.

5. *Protozoa*. These are microscopic, one-celled animals, varying greatly in size and shape. They are motile, that is, are able to move about in quest for food. Some are jelly-like masses that flow sluggishly and engulf their food, and others are propelled by hair-like appendages. They are parasites, living for the most part on bacteria; but some attack larger hosts and even cause diseases in man, such as malaria, African sleeping-sickness, and almost certainly yellow fever.

CHAPTER XVIII

THE CHEMICAL WORK OF MICRO-ORGANISMS

IF WE examine a sample of fertile garden soil with a microscope we discover it to be a very complicated mixture: rounded grains of quartz, flakes of mica, particles of silicate minerals in all stages of weathering, root-hairs and fragments of decaying wood. All these coarser particles are plastered over with a dark gelatinous colloidal film, in which adhere smaller particles just visible with the microscope: bits of clay, granules of ferric oxide, isolated plant cells, protozoa, fungus threads, rods, spores and filaments of bacteria. A fertile soil is a swarming universe, containing thousands or millions of living inhabitants in a sample as large as a grain of wheat.

The Life in the Soil

We may regard the coarser particles of a soil as the soil framework. The life is in the gelatinous film that the framework supports. This consists in part of water-absorbing particles that have been weathered away from the crystalline minerals in the larger grains of soil, and in part of gelatinous organic colloids (humus) that are produced when dead plant material is broken down by the onslaughts of bacteria and fungi. This colloidal film holds most of the water that is needed for growing crops. When rain falls, the colloids drink it in, and swell enormously; then, during the dry season, they slowly yield it up. Any moisture that may be present beyond the ca-

capacity of the colloids to absorb forms a film of liquid "soil solution" surrounding the solid particles of soil.

In seasons of drouth the colloids harden and shrink, and the life in the soil lies dormant. Bacteria form spores, to await happier conditions. Then, when moisture comes again, there is a veritable resurrection. Spores burst into life, bacteria multiply amazingly, protozoa swarm like sharks in the liquid films, fungi thrust their filaments through all the porous mass, and every living cell engages with delight in its own favorite form of chemical activity. Competition is keen. Only the fit survive. So, presently, we have a biological equilibrium in which every type of organism has won all the ground that it has the force to maintain in competition with the rest. As a rule, no newcomer has any chance to gain a foothold and hang on, in the face of such rivalry.

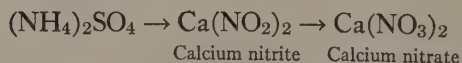
A sample of soil under the microscope demonstrates that different sorts of soil particles favor different sorts of organisms. A fragment of decaying wood will be overgrown with mold, and the soil in its immediate neighborhood will be tenanted by the particular sorts of bacteria that are able to endure the acids produced from the organic matter of the wood. A fragment of limestone, on the other hand, will neutralize the acids in its immediate neighborhood, and so will favor the growth of organisms that must have a nearly neutral environment. Moreover, the surface of the soil is the special habitat of organisms such as the algae, which must have sunlight; from the surface downward to depths of a few inches flourish "aerobic" organisms, which need a plentiful supply of free oxygen for carrying out processes of oxidation; and at great depths, we find others ("anaerobic") which thrive in the nearly complete absence of free oxygen, and which are often injured by exposure to the concentrations of oxygen that approach those of ordinary air.

Among the bacteria are some which are as famous as tares and thistles for their ability to carry on in the most discouraging situations. These are the autotrophic bacteria. They have no need of sunlight, organic matter, or any sort of assistance from other organisms. Most soils contain a few species of bacteria of this class. Given a supply of inorganic materials, including something they can oxidize to obtain energy, they will fall to work with a will, building the inorganic elements of carbonates, phosphates, sulfates and nitrates into complex living protoplasm.

Among the most interesting of these autotrophic or self-energizing bacteria are the sulfur bacteria, which derive their energy by oxidizing hydrogen sulfide to produce water and sulfur. The microscope can easily distinguish granules of sulfur within the bacterial cells; and there is reason to suppose that the largest and most important deposits of sulfur in Nature have resulted from the activities of organisms of this type. There are other bacteria which can oxidize elementary sulfur, to produce sulfates.

Now and then other autotrophic bacteria win public notice by clogging up the water mains of a city. These are the iron bacteria, which derive their energy by oxidizing ferrous salts to ferric oxide. This may accumulate in such quantities as to close the smaller distributing mains. Yet it seems probable that these same organisms were responsible for the accumulation of our most important beds of iron ore. In ancient lakes, ages before man appeared on the earth, our microscopic friends were busily at work accumulating the materials that have given us an industrial civilization.

Finally, we ought to mention the nitrifying bacteria, which obtain their energy by oxidizing ammonium salts, in two stages—first producing nitrites, then nitrates:



These two steps are carried on by two entirely distinct groups of bacteria, which are found in most soils, and which can be isolated and studied by methods based on those invented by Pasteur and Koch.

BACTERIA IN AGRICULTURE

The autotrophic bacteria are all devoted to the up-building of organic compounds at the expense of energy derived from the oxidation of inorganic materials. Yet most of the bacteria of the soil are engaged in tearing down. When plant or animal matter decays, the proteins and other nitrogen compounds that it contains are resolved into simpler and simpler types of molecules. Eventually, ammonia is produced; hence the bacteria that take part in these final stages of decay are called the ammonifying bacteria. Putrefaction, on the contrary, takes place in the presence of a more limited supply of oxygen, and organisms of a different type carry on the work of destruction, producing complex organic compounds having offensive odors.

Nitrogen passes through a cycle of changes, as the result of the chemical activities of plants, animals and bacteria. The continuance of life upon the earth is dependent on this cycle and therefore on micro-organisms. Yet the total combined nitrogen in nature, at any moment, is relatively small. If we could compel the individual molecules of nitrogen in the air we breathe to relate their personal histories, we should doubtless discover many which have been drifting with the winds since the earth came into being, without ever having taken any part in life. In Fig. 14, on the next page:

1. The nitrates of the soil are absorbed through the roots of growing plants and converted into plant protein. In this sentence we summarize a highly complicated process whose details we have hardly begun to understand.

It is as if we said that a factory absorbs steel, felt, wood and ivory and converts these materials into pianos.

2. Plant protein is digested and absorbed by animals, and thus becomes animal protein—here again an exquisitely elaborate process.

3. Animal protein is broken down, as a result of the animal's vital activities, and the nitrogen contained in it is excreted as urea or a related compound.

4. Dead plant and animal material is torn down by bacteria, in the processes of decay and putrefaction, and the final stages are carried out by the *ammonifying bacteria*, producing ammonia.

5. Ammonia is then oxidized, first to nitrites, then to nitrates, by the *nitrifying bacteria*. Thus the cycle is completed, and nitrogen is restored to a state that can be used by a new generation of plants.

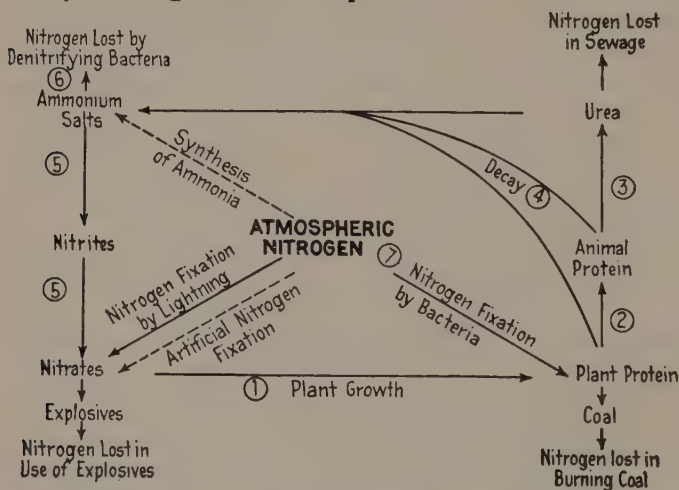
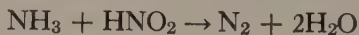


FIG. 14. THE NITROGEN CYCLE.

But there are some other processes to consider:

6. Occasionally, when soil is heavily manured, ammonia reacts with nitrites to produce elementary nitrogen:



Denitrifying bacteria may be responsible for this change. This elementary nitrogen is restored to the atmosphere, and is lost to agriculture. The process is called *denitrification*. It is a "leak in the nitrogen cycle." Fortunately, it is offset by other processes, known as *nitrogen fixation*, that bring atmospheric nitrogen into combination with hydrogen or oxygen and so make it available for plant growth.

7. Certain bacteria have the ability to bring atmospheric nitrogen into combination with other elements to construct protoplasm. The most famous of these *nitrogen-fixing bacteria* are those that are found in nodules on the roots of leguminous plants such as clover, peas and alfalfa.

Wherever leguminous plants grow luxuriantly their roots will be found covered with nodules, from the size of a pin point to the size of a man's thumb.

**Nitrogen-
Fixing
Bacteria**

Under the microscope, the nodules are discovered to be modified rootlets, in which many cells are swarming with bacteria.

One might readily consider such an invasion of bacteria to be a menace to the very existence of a plant. Yet, strange to say, the legumes that have been infected always grow much more luxuriantly than those that have not.

The nodule-forming bacteria, then, are not parasites. They are not blood-thirsty pirates but honest traders, engaged in a fair exchange. For the leguminous plant, spreading its green antenna to receive the wireless signals from the sun, absorbs so much energy that it can build up more carbohydrate than it needs. Yet it is hungry for nitrogen. The ocean of atmospheric nitrogen with which it is surrounded is no more fit for its use than an ocean of salt water is to slake the thirst of sailors. So an exchange is arranged. The plant offers its surplus carbohydrate to the bacteria, which derive energy by tearing the carbohydrate down; and in return, the bacteria bring atmospheric nitrogen into combination with other elements

to form nitrogen compounds, which are handed over to the plant.

Just how this exchange is carried out is not yet clear. Perhaps the bacteria secrete enzymes which enable the plant itself to couple the reactions in which carbohydrate is torn down with those in which nitrogen compounds are built up. Or the bacteria may carry on the work within their own bodies and secrete nitrogen compounds which the plant can use. More probably the plant has to wait until the bacterial cells die before it can step in and claim the products of their labor.

It seems likely that different legumes are associated with different species or strains of bacteria, for it is known that a culture of bacteria from the nodules of clover or alfalfa will not inoculate a very different legume, such as the soy bean. Agricultural stations now supply cultures of bacteria for different sorts of legumes; and fields in the United States and Canada that have not responded to liming or to fertilizers, have often been greatly improved by inoculation with a culture suited to the crop to be grown. This is probably the only instance in which crops have been benefited by adding pure cultures of bacteria to the soil. Attempts, for example, to hasten the production of nitrates in the soil by adding cultures of nitrifying bacteria have always failed, doubtless because these bacteria are present in all soils, and fail to prosper only when the soil conditions are not suited to their growth. Indeed, in the Old World, where the land has been cropped for centuries, most soils have already become inoculated with nodule bacteria, and further inoculation is without results.

The nodule bacteria are not the only micro-organisms that can fix nitrogen. A few molds, associated with the roots of certain plants, such as the alder, are believed to be able to do the same thing. It has recently been discovered, also, that certain peculiar "glands" in some leaves

are really structures filled with nitrogen-fixing bacteria, which may or may not be related to those that produce nodules on the rootlets of legumes. Most soils, moreover, contain bacteria of other sorts, which can be cultivated in solutions that are free from nitrogen, and can fix nitrogen from the atmosphere at the expense of energy derived by oxidizing sugar. Such species may have an important part in building up the fertility of the soil, during the course of centuries; yet the nodule bacteria are of far more importance in practical agriculture.

Every crop that is harvested produces vast quantities of waste material that must be disposed of in some way.

The Carbon Cycle

Fortunately, this waste material need not often be burned. If it is plowed under or permitted to lie on the surface of the land, it disappears in the process of slow combustion that we call decay. The underground parts of our common harvested crops often extend downward to distances of ten feet or more. In a few years the soil would be so clogged with roots as to prevent further crops from being raised, did not decay clear away these accumulations.

It used to be supposed that complex organic matter would somehow decompose of its own accord, as soon as the life that produced it had become extinct. But about the year 1880 it was discovered that fruit and vegetables that have been boiled, and then hermetically sealed to exclude micro-organisms, will usually keep indefinitely. We now understand that decay is the work of micro-organisms. The fungi usually lead the attacks, forcing their way through the dead material, from cell to cell, with the aid of enzymes which they secrete to break down the cell walls. Then, when the whole structure is thoroughly riddled, bacteria swarm in and speedily reduce the material to a structureless colloidal mass of humus. Finally, other bacteria break down the humus itself, pro-

ducing organic acids, and eventually carbon dioxide and water.

Thus the carbon in nature, like the nitrogen, passes through a cycle (Fig. 15):

1. Beginning as carbon dioxide, it is elaborated into living plant material under the influence of the sun's rays, in the process of photosynthesis.

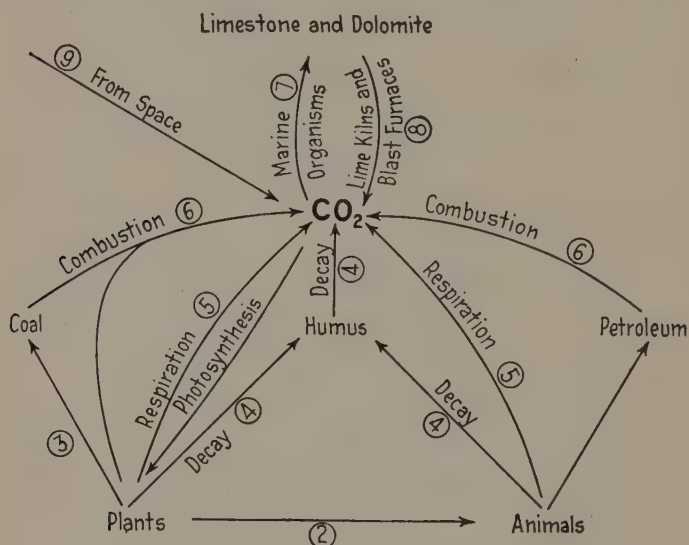


FIG. 15. THE CARBON CYCLE.

2. Plant material may be eaten by animals, which work it over to produce new compounds in the processes of digestion.

3. In the past, vast quantities of plant material have been converted into coal under the influence of heat and pressure, during the course of geological ages.

- | | |
|---|---|
| 4. Decay | } All return carbon dioxide to the atmosphere, whence it originally came. |
| 5. Respiration of plants and animals | |
| 6. Combustion of wood, coal and petroleum | |

7. An immense store of carbon dioxide is dissolved in the ocean. Marine organisms constantly withdraw this to form deposits of chalk, limestone and dolomite, which may be locked up in the depths of the earth indefinitely. This process would eventually exhaust the supply of carbon dioxide in the atmosphere and ocean, and so put an end to life on the earth. However, there are two other processes which tend to make good this loss, and which may offset it completely:

8. Limestone is decomposed in lime-kilns and blast furnaces, and through the action of plant acids on limestone particles of the soil.

9. Carbon dioxide arrives from space. Our earth is still gathering in solid particles and stray molecules that it meets on its journey through space; in other words, it is continuing to grow by the process by which it probably came into being.

The preceding discussion has shown how the practical management of a farm and the problems of soil fertility

**Bacteria and
Permanent
Soil
Fertility**

are complicated by the activities of bacteria. The most evident purposes of cultivation are to kill weeds, favor the spread of roots, and reduce evaporation from the surface of the soil. Yet its effects on the soil bacteria are likewise important. Cultivation aerates the soil, and so stimulates the bacteria that require oxygen for their work. Decay and nitrification are speeded up enormously. Carbon dioxide is produced in quantity, by the oxidation of organic material, and helps to dissolve the minerals of the soil, particularly limestone. Thus cultivation may increase the amount of the soluble inorganic mineral nutrients in the soil.

Yet these benefits are not to be obtained apart from serious dangers. When nitrates are produced more rapidly than plants can use them, they are apt to be leached from the soil by rain. When the bacteria of decay are too much encouraged, they may destroy the soil's store

of organic colloidal matter (humus), which is so important for conserving moisture, and on which the life in the soil depends. When carbon dioxide is produced too rapidly, as a result of the activity of the bacteria of decay, a great deal of calcium and magnesium may be dissolved and lost by leaching. There is no doubt that evils such as these, particularly the destruction of humus, have made many cultivated soils become infertile; and are even now at work decreasing the fertility of many important agricultural regions of the world, such as the American Middle West.

The problem of permanent soil fertility, therefore, is something more than a problem of devising means to restore the mineral nutrients, such as potash and phosphorus, that are taken out by growing crops. Humus must be conserved or increased. The colloids of the soil must be brought to a condition favorable for tillage, for conserving moisture, and for maintaining the activity of the soil bacteria. Losses by leaching and erosion must be guarded against. Nitrogen fixation must be provided for, when possible, by including legumes in a rotation of crops, and by seeing that conditions are right for the development of the nitrogen-fixing bacteria. The bacteria of decay, the ammonifying and the nitrifying bacteria must be encouraged, yet kept within bounds. This means that one must consider the effect of soil reaction (whether acid, neutral or faintly alkaline) in determining what sort of bacteria shall flourish. One must pay heed to all that is known or becoming known concerning the effects of different crops and different kinds of fertilizers on the activity of the soil bacteria. Finally, undesirable micro-organisms must sometimes be destroyed by applying soil disinfectants, in order that helpful bacteria may flourish. Liebig once remarked that agriculture is the richest of all the practical arts in principles to be applied, but the poorest of all in the general understanding of those principles.

FERMENTATION

When yeasts were first discovered and shown to be necessary to the alcoholic fermentation of sugar (1837), their mode of action was by no means clear. It was at first supposed that the yeast built up unstable compounds which later decomposed, causing molecules of sugar to decompose—just as a fire, kindled in shavings, may ignite lumps of coal. Nearly fifty years passed before Pasteur and others demonstrated that fermentation was a part of the life processes or vital activities of the yeast. The yeast plant couples a chemical reaction in which complex sugar molecules are torn down with reactions in which the complex molecules of its own protoplasm are built up. It compels the one process to supply the energy that the other process needs, just as a descending weight may be made to wind up a spring. Human chemical ingenuity has never accomplished anything of this sort. If we tear down complex molecules in the laboratory, energy is released as heat, and that is the end of it.

Finally, in 1897, a German chemist, Buchner, dried some yeast at room temperature, ground it with sand in a mortar, extracted the ground material with water, and filtered the extract through very finely grained filters of baked clay. He obtained a liquid which was completely free from yeast cells, yet which would cause sugar solutions to ferment. Thus it was made plain that the yeast cells contain some organic substance which is set free when the cells are broken down by grinding, and which acts as a catalyzer, causing sugar to decompose to form carbon dioxide and alcohol.

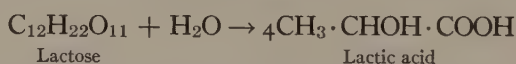
Many such organic catalyzers or “soluble ferments” are now known, which are produced by bacteria and by living plants and animals, and which serve to carry on reactions that would not otherwise take place. As a class, they are now called *enzymes* (Greek: in leaven). The

particular enzyme that is responsible for converting glucose into carbon dioxide and alcohol is called *zymase*. The varied chemical activities of bacteria are carried on by enzymes, and others play a part in the growth of plants and in the digestion of foods by animals. Some enzymes carry on their work within the cells in which they are formed, and are released only when the cell walls are broken down, as in Buchner's experiment in grinding dried yeast with sand. Others are secreted through the cell walls, and act upon materials outside the cell.

Most enzymes are destroyed by heating or by slight concentrations of alkali. None of them has ever been obtained in a pure condition, and their chemical composition is still a complete mystery. Since the chemical changes they induce are of the most diverse sorts, it seems probable that they are of the most diverse constitutions.

The term fermentation may be applied, in a loose sort of way, to *any chemical change that is brought about under the influence of micro-organisms or of enzymes secreted by them*. One of the most interesting and important of these is lactic fermentation of milk. Bacteria are present in all normal milk, which can ferment milk sugar (lactose):

Lactic Acid
Fermentation

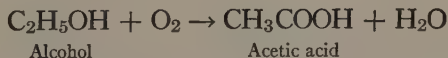


This change will take place in the complete absence of oxygen. When the lactic acid has accumulated to a sufficient concentration, it causes the casein of the milk to coagulate or settle as a semi-solid clot or curd. This, or a clotting produced by rennin, is the first stage of cheese-making. But other organisms commonly take part in the clotting process, and alter the composition or texture of the curd; and in the final stage or "ripening" of the cheese, water is lost, the curd acquires a firmer consistency, and

special flavors and aromas are developed by the action of molds and other micro-organisms. Different varieties of cheese are ripened under different conditions, or with cultures of different organisms.

Lactic acid bacteria are commonly present in commercial yeast preparations and in dough, and play a part in the leavening process, improving the flavor and the keeping qualities of the bread. Some bakers add a little lactic acid to dough for the same purpose. In making sauerkraut or silage, the finely chopped green vegetable material, containing considerable amounts of starches or sugars, is tightly packed in a container, so that very little air can enter. Some alcoholic fermentation may take place; but presently the lactic acid organisms get the upper hand, and produce such a high concentration of acid that other bacteria are suppressed. The material will then keep almost indefinitely, except that the presence of air in the upper layers may permit acid-resistant molds to flourish there.

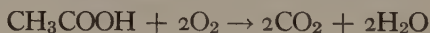
Since prehistoric times it has been known that wines exposed to the air become covered with a thin skin or membrane, and quickly turn sour. The wine has turned to vinegar, which is impure, dilute acetic acid. Pasteur improved the ancient methods of producing vinegar, and made the first of a long series of researches which have shown that a great many different bacteria are able to oxidize alcohol to produce acetic acid:



The oxygen needed for this process commonly comes from the air, hence the bacteria responsible for acetic fermentation usually flourish best at the surface of the liquid, and there accumulate until they form a continuous membrane. But there are other bacteria that can oxidize

alcohol in the nearly complete absence of air, provided carbohydrate is present to serve as a source of oxygen.

When fruit or grapes are crushed and exposed to the air, alcoholic fermentation usually takes place, under the influence of the wild yeasts that are scattered everywhere by the winds. Then, when most of the sugar has been turned to alcohol, bacteria usually step in and produce vinegar. Yet the vinegar so obtained is of uncertain flavor, since it is produced by organisms of uncertain identity. Moreover, it is now known that some of the acetic bacteria work much more rapidly than others. Vinegar is therefore now usually prepared from apple juice or molasses, by carrying out the alcoholic fermentation with a pure culture of yeast, then permitting the alcoholic liquor to trickle over beechwood shavings or similar material that is covered with a growth of acetic bacteria. By insuring the right sort of bacteria, a favorable temperature, and plenty of air, vinegar is produced in a few hours, though the older methods required days or weeks. The process must be stopped at the right time, else other bacteria may carry the oxidation further, converting acetic acid to carbon dioxide and water:



Ethyl alcohol has so many industrial uses that its production by fermentation would still be a very important industry even though its use as a beverage were eliminated. The raw material to be fermented may be grain, fruit, tubers, cane or beet molasses—in fact almost any material rich in starch or sugar. Even sawdust may be hydrolyzed by dilute sulfuric acid, producing fermentable substances (p. 174).

The general procedure followed in preparing alcohol depends on the raw material that is to be used. If the raw material is starch (grains or tubers) this must

**Production
of Alcohol
by Fermenta-
tion**

be converted into sugars before it can be fermented. The material is ground and heated with water, then treated with malt (sprouted barley), which contains an enzyme that converts the starch into glucose and maltose. If the raw material is sugar, the preliminary step with malt is unnecessary; for even though cane sugar is not directly fermentable, most strains of yeast secrete an enzyme that slowly converts it into glucose and fructose. Yeast, then, is added at the proper temperature; and derives the energy for its growth by the decomposition of sugar withdrawn from the solution.

The chief products of alcoholic fermentation are ethyl alcohol and carbon dioxide:



Glucose

but small quantities of the other alcohols, glycerol, acids and esters are always produced. The total productive capacity of fermentation plants in the United States, in 1929, was about 220,000,000 wine gallons from molasses and 15,000,000 wine gallons from grain. The industrial demand for alcohol is about 100,000,000 wine gallons.

Bacterial fermentations are known in which butyric, citric, oxalic and other organic acids are produced. Com-

Other Types of Fermentation plex fermentations are involved in the earlier stages of turning hides into leather, and in preparing linen from the fibers of the flax plant (p. 175).

In recent years a study has been made of the chemical activities of special varieties of bacteria and special strains of yeast. Some of them produce the higher alcohols (fusel oil) as a principal product, and ethyl alcohol as a mere by-product. During the World War a Canadian plant produced 200 tons of acetone a month by the fermentation of corn and potatoes. Recently a method of

fermentation has been developed and operated commercially on a small scale, in which glycerol appears among the principal products of the fermentation of sugar. A ton of cane sugar produces about 400 pounds of glycerol, 550 pounds of alcohol, 100 pounds of mixed aldehydes, most of the remainder being gaseous products, chiefly carbon dioxide.

The most important higher alcohol is butanol, C_4H_9OH . This is used in the preparation of butyl acetate, which is of great commercial value as a solvent in the preparation of nitrocellulose lacquers. Butanol and acetone are now manufactured on a large scale by a process of bacterial fermentation, using corn mash as a raw material. Spores of Weizmann bacteria are used, and extreme precautions taken to prevent foreign organisms from entering. The fermentation produces about 60 parts of butanol to 30 of acetone and 10 of ethyl alcohol, together with a mixture of carbon dioxide and hydrogen gases in about equal volumes. Elaborate methods have been developed for sterilizing vessels and pipes by high pressure steam. Liquids are circulated by pumps having pistons that work in packing sterilized by phenol. One plant of the Commercial Solvents Corporation has a capacity of 30,000 bushels of corn a day. There are 148 fermentation vessels, each of 40,000 gallons capacity, and during the production of butanol by fermentation, 150,000 cubic feet of mixed carbon dioxide and hydrogen gases are produced each day as a by-product of the bacterial action. The carbon dioxide is of course readily liquefied, or it may be put on the market in the solid form as a refrigerant. The alert management of this particular concern provided means for saving the hydrogen as well, by combining it with nitrogen to form ammonia, in a plant having a capacity of 24 tons of liquid ammonia a day; and recently a plant has been set up for combining hydrogen with carbon monoxide to produce methanol, by the catalytic method we have previously men-

tioned (p. 219). At the present moment the production of butanol and acetone is probably the best example that is to be found anywhere of the application of bacteria on a commercial scale. As a piece of bacteriological engineering it is unique. In 1929 it produced about 25,000 tons of butanol alone.



Courtesy of Commercial Solvents Corporation.

THE PRODUCTION OF BUTANOL BY FERMENTATION

This shows the upper level of the fermentation vessels.

Large quantities of corn oil and corn germ meal are marketed as by-products of this fermentation process. New uses for the chief product, butanol, are constantly being discovered. Butyl acetate is only one of several commercially important derivatives of this alcohol, including butyl phthalate, which is an important plasticizer for cellulose esters (p. 188).

CHAPTER XIX

ROOTLETS AND GREEN LEAVES

**Specializa-
tion** Most bacterial cells have no separate parts that are distinguishable by direct observation or by staining; but within the cells of algae there may be found a nucleus, threads and granules of different sorts, and sometimes oily droplets; and among the higher plants different kinds of cells are built into special tissues, which are set aside for special uses. The higher plants have ramifications underground, which grow vigorously, pushing aside the particles of soil, sending forth a myriad rootlets in a greedy search for nutrients, and striking downward to great depths to find a supply of water. Above ground, a branching stem supports a multitude of green leaves, in which the most amazing chemical transformations are attuned to pulses in the ether that have their origin in the turmoil of electrons in the gases of the sun. The flowering parts of plants and, finally, the seeds and fruit are leaves that have been modified to serve for reproduction. Thus the higher plants are distinguished by specialization, in which different organs are developed to serve different chemical and mechanical uses.

**Chemical
Activities
of Plants** In their constructive activities, the higher plants are not so different from micro-organisms. They are merely more versatile. A single species, with its multitude of specialized tissues, may undertake more different sorts of chemical synthesis than are possible to any one kind of micro-organism. The higher plants (and the algae)

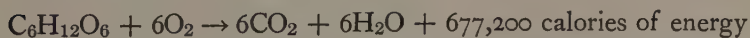
nevertheless have a great advantage over the rest of the plant world in being able to make use of the sunlight as a source of energy. They synthesize carbohydrates from carbon dioxide and water, at the expense of the energy of sunlight. This process, *photosynthesis*, is a reduction process, in which carbon dioxide is compelled to part with some of its oxygen to produce substances that will burn. When the final product is glucose, the reaction may be formulated:



The organic compounds thus produced are removed to other parts of the plant to meet immediate demands for energy or to be stored away for future use. This is the process of *translocation*. It calls for chemical changes, since insoluble deposits of starch need to be converted into soluble sugars before they can be transported; and when they have reached their destinations in distant portions of the plant, they may need to be reconverted into starch, inulin or cellulose.

In all parts of the plant are general synthetic activities in which organic compounds other than carbohydrates are produced: glucosides, tannins, acids, alkaloids, proteins, fats, pigments and a multitude of other substances. These constructive operations include those in which the mineral nutrients absorbed by the roots are built into organic compounds.

The energy that is needed for these operations is derived by oxidizing carbohydrates. This is accomplished by the process of *respiration*. It is interesting to notice that both plants and animals derive most of their energy by the oxidation of glucose:



Respiration thus tends to undo the work of photosynthesis, for it is chemically the reverse of photosynthesis.

Yet photosynthesis predominates in plants, when it takes place at all. The higher plants create more organic matter than they destroy, and produce a surplus for the support of animals and man. The fungi and bacteria, on the other hand, often tear down hundreds of times as much organic matter as they produce.

We have seen that bacteria play an important part in making the soil fit for the growth of the higher plants.

**Selective
Absorption**

They sweep away the burden of organic matter bequeathed by former generations of plants, and restore the mineral nutrients to a condition fit to support new life. The nitrogen of complex organic compounds is converted into ammonia and, ultimately, into nitrates. Moreover, the bacteria swarm into every crevice into which water can penetrate, and lend help in tearing down the most stubborn rocks. It is a matter of chemical equilibrium. A mineral may be but slightly soluble, yet at length will dissolve completely, if a part of the dissolved material is continuously withdrawn to construct bacterial protoplasm.

PLANTS AND MINERAL NUTRIENTS

The moisture of the soil enters through the walls of the root cells. Yet note! It is not pure water that flows in, but a solution, containing the mineral nutrients that the plant needs for its growth. At that point there is selection. The cell wall is a physiological Ellis Island, which admits the immigrant ions * that are most desired and turns back the rest. The reverse process, too, is under control. The cell wall often permits enzymes to escape and carry on their activities outside the cell. Carbohydrates, as well, are often moved outward in large quantities and translocated to other parts of the plant. Yet

* An ion is an electrically charged atom or group of atoms. Because of its electric charge it is enabled to lead an independent existence as if it were a molecule.

the cell wall is constantly on guard to retain the ingredients of the living protoplasm. These shall not pass!

This is not a matter of separation by dialysis, for colloids sometimes pass through while crystalloids are held back. The chemical properties of the protoplasm are doubtless responsible, since selective absorption takes place with organisms that have no cell wall. Yet very little is known about the details of the process. At the very portal through which the mineral nutrients pass to play their part in the processes of life, we meet the first of the mysteries of life.

But what are the mineral nutrients which are selectively absorbed by the root hairs and then passed on from cell

**The Mineral
Nutrients**

to cell, each to its own proper destination?

Which inorganic elements are necessary to plant growth? One might hope to form a rough idea by burning the plant and noting which elements are left in the ash. For when a plant is burned, most of its carbon, nitrogen, hydrogen and oxygen, and a part of its sulfur and chlorine are carried away as gaseous products, while the other elements remain. Actually, plant ashes consist largely of potassium carbonate, with smaller amounts of calcium and magnesium carbonate and phosphate, together with some silica and other inorganic compounds.

Yet this does not show which elements a plant really needs, but merely which it is willing to absorb. One can not argue a physiological need for alcohol from a man's willingness to drink it. The experiments that definitely identified the essential mineral nutrients were performed in 1851 by a French chemist, Boussingault, who found that many plants can be made to grow in vessels containing solutions of mineral salts in distilled water. Yet certain elements had to be present if the plant was to flourish, no matter how plentiful the supply of other elements. The necessary mineral nutrients, absorbed through the roots of plants, were found to be:

Four metals: Potassium, calcium, magnesium, iron.

Five non-metals: Nitrogen, phosphorus, sulfur, hydrogen, oxygen.

Incidentally, these "water cultures" of Boussingault confirmed the conclusion of preceding workers, who had shown that carbon, the most plentiful element in plants, is not derived by green plants from the carbonates or humus of the soil, but must come from the atmosphere.

In addition to these necessary elements, there are some (silicon, aluminum, sodium, chlorine) that are found in the ashes of nearly all plants; and a few others which are present in individual species. These elements have often been assumed to be accidental and non-essential, but it is very probable that they may perform some of the duties which the essential elements would otherwise have to perform. Moreover, recent experiments have shown that plants may demand mere traces of these or other elements, such as manganese, vanadium and boron, for proper growth and reproduction. That this remained unsuspected during the three-quarters of a century that elapsed after the work of Boussingault may be attributed to the fact that investigators failed to use salts of tested purity. Much of the older work will have to be repeated, with more than usual care and pains.

Of the different mineral elements that have been recognized as necessary for the growth of plants, all but
Fertilizers potassium, nitrogen and phosphorus, and
 occasionally calcium and sulfur, occur as soluble compounds in all soils in sufficient quantities for the growth of crops. Liebig and others thought that the problem of maintaining a soil in permanent fertility was merely one of supplying the elements (particularly potassium, nitrogen and phosphorus) that it happened to lack. It seemed reasonable to suppose that one might analyze a soil to discover which elements were present in too small amounts, or might analyze the ashes of a

crop to determine which elements were being removed from the soil, and then prescribe accordingly.

It was the age when the systematic methods of inorganic chemistry had just been developed by Berzelius, Fresenius and others. Enthusiasm ran riot. Thousands of soils in all parts of the world were analyzed and classified, and a great fertilizer industry was built up, to supply the needs of soils as revealed by chemical analysis and tests with growing crops in experimental plots.

Then, slowly, it was discovered that something was wrong. Prescriptions based on analyses of soil or ashes were frequently of doubtful value. Soils that appeared to contain plenty of calcium were often immensely benefited by the application of ground limestone. Soils that contained very small amounts of nitrates were sometimes very productive.

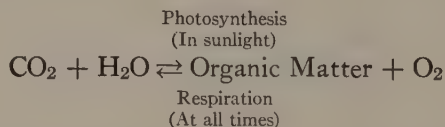
We now understand that the mineral nutrient theory of Liebig was far from suggesting all the effects that are produced when fertilizers are applied to the soil. Mineral nutrients are supplied to the crop, truly enough. But, in addition, the properties of the colloids of the soil are modified, according to the ions that the fertilizer contains. Again, all the bacterial activities are altered. For example, if you apply sodium nitrate to a soil you tend to hinder nitrification; you invite bacteria that reduce nitrates to nitrites in order to obtain oxygen; you favor micro-organisms of the soil that are tolerant of sodium or that can make use of the nitrogen of nitrates in building their own protoplasm. A load of mineral fertilizer may make over the microscopic flora in a most startling way, as if a forest had been swept away by a fire and replaced by prairie grass.

Finally, one should consider the special needs of each crop for mineral nutrients, and the effect of fertilizers on the physical characteristics and ripening season of plants. The farmer may also make the unpleasant discovery that a fertilizer stimulates the growth of troublesome weeds.

Altogether, the effect of fertilizers on crops is so complex as to defy exact analysis. We have to rely on field experiments, performed with the greatest discrimination and judgment, with a careful consideration of the effect of uncontrolled variables. Even experienced investigators have sometimes made mistakes, as in applying potassium sulfate to a crop, and ascribing an increased yield to potash when it was really due to sulfate.

PHOTOSYNTHESIS

Priestley and Scheele both made observations on the relation of the atmosphere to the growth of plants. They arrived at opposite conclusions, for the reason, as we now may guess, that one of them observed plants which were growing in bright sunlight; and the other, plants which were in diffused light or in the dark. The truth was discovered by Ingen-Housz, a Dutch physician, in 1779. It was found that when green leaves are in the sunlight they absorb carbon dioxide from the air and give off oxygen; but that *all* parts of plants, especially their flowers, fruits and tubers, whether in sunlight or in the dark, engage at the same time in the reverse process, absorbing oxygen and giving off carbon dioxide. In the sunlight, the former process predominates in green leaves. In dim light of a certain intensity the two processes just balance.



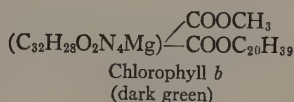
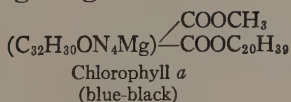
Ingen-Housz saw clearly that plants absorb carbon dioxide and produce organic matter and oxygen; and that animals use the organic matter of plants as food in constructing animal tissue, which is finally torn down and

exhaled as carbon dioxide, in respiration, to serve again for the support of plants. These observations were the more remarkable in being made five years before Lavoisier published his famous work on respiration and combustion.

A generation later a French chemist, de Saussure, (1802) showed that only the green parts of plants absorb the carbon dioxide; that plants grow more rapidly if the supply of this element in the air is somewhat increased, but that too much of it is injurious; that carbon monoxide, as a rule, can not replace carbon dioxide; and that plants need oxygen as well as carbon dioxide.

Other observers added other details. It was found that it is not the heat rays of the sun, but the light rays, that cause carbon dioxide to be absorbed—especially the red part of the spectrum. The carbon dioxide enters most leaves through microscopic openings, which have been named *stomata*. These are provided with guard cells that permit them to be opened and closed, to suit the demand for carbon dioxide or the amount of moisture in the air. It was found that green leaves which have been kept in the dark produce starch in a few minutes when they are restored to the light. Gradually, it became clear that chlorophyll, the green coloring matter of leaves, serves as a catalyzer in the reactions in which organic matter is produced.

Yet chlorophyll is more than a mere catalyzer. It is a carrier of energy. Though we still have no clue to the manner in which it serves the plant in photosynthesis, we do know something of its chemical composition. It has recently been shown to be a mixture of two amorphous (non-crystalline) pigments, both of which are complex organic compounds containing magnesium:



Since both these compounds contain —COOR groups they are to be classed as esters (p. 120). They are not magnesium salts; that is, they do not answer to the usual tests for magnesium-ion, Mg^{++} . The magnesium atom is a part of a complex organic group, and is probably directly connected with nitrogen. The details of structure of the part of the molecule that is included within the parentheses above, as we have written the formula, still remain to be determined.

The two chlorophylls are always associated in plants with two yellow pigments, and sometimes a red-brown pigment as well. Plants which have yellowish or reddish foliage do not lack chlorophyll, but merely have so much of the other pigments as to conceal it. When leaves die in autumn, the carbohydrates of the leaves ferment and enzymes tear down the chlorophyll and produce new pigments of different colors and unknown composition.

The chemical transformations of photosynthesis are carried on in structures called *chloroplasts*, which are scattered through the leaf cells. They are usually small and of an ovoid shape and contain a complex mixture of colorless gelatinous material, together with chlorophyll and other pigments, starch, and oily droplets. A single cell may contain one or many chloroplasts. When the sun shines upon the chloroplasts they absorb carbon dioxide, give off oxygen, and produce soluble sugars and ultimately starch.

The rate at which the chloroplasts synthesize organic matter depends on the wave-length and intensity of the light, the concentration of carbon dioxide in the atmosphere, the number of chloroplasts, the amount of chlorophyll that they contain, the temperature, and numerous other factors. For most plants, a temperature between 30° and 40° C. is most favorable to photosynthesis.

Sun-loving plants are the most active in converting carbon dioxide into organic matter. A square millimeter of

**The Work
of the
Chloroplasts**

sunflower leaf may contain 600 stomata and 500,000 chloroplasts actively engaged in photosynthesis. Thus a medium-sized leaf (30 square inches) may have 12,000,000 stomata and 10,000,000,000 chloroplasts. Such a leaf may absorb 4 cubic inches of carbon dioxide per hour. From this it may be calculated that a single chloroplast can absorb and transform about 44,000,000 molecules of carbon dioxide every second!

The equation on page 272 shows only the original reactants and final resultants of a series of chemical changes, leading from carbon dioxide, water and energy to oxygen and sugars or starch. The intermediate steps are still unknown, in spite of the efforts of scores of chemists during almost a century. The chloroplasts have guarded their secret well.

Some chemists have believed that the carbon dioxide is first reduced to formaldehyde, HCHO , or formic acid, HCOOH . Traces of both these substances can indeed be detected in green leaves, and both of them can be converted into simple sugars by artificial means. Yet this proves little, since both of them are found in plant material that is devoid of chlorophyll, and in the leaves themselves may be formed by the decomposition of other substances that leaves contain. Moreover, the conditions under which they have been converted into sugars are not at all the conditions that obtain in green leaves. For that matter, there are dozens of simple organic compounds that can be converted into sugars, if one puts no restrictions on the methods to be employed.

Many efforts have been made to produce carbohydrates from carbon dioxide by artificial means, without the aid of green plants. When dilute solutions of carbon dioxide, in the presence or absence of other substances, are acted upon by ultra-violet light, traces of formic acid, and perhaps of formaldehyde, have been obtained. In

Intermediate
Products
in Photo-
synthesis

Photosyn-
thesis in the
Laboratory

other experiments, formic acid and formaldehyde have been converted into sugars or near relatives of sugars, under the influence of ultra-violet light or of sunlight. Nevertheless, these reactions are very incomplete, and the carbohydrates obtained are not the ones that are important in plants. Plants, in fact, do not use ultra-violet light in photosynthesis, but *visible* light, chiefly in the red region of the spectrum. Photosynthesis in the laboratory, as a practical means of producing carbohydrates, is still a dream of the future.

Poe long ago complained that science had "driven the hamadryad from her grove." By this he meant that science tends to deprive nature of its romantic mystery. Yet we have seen that there is mystery enough in photosynthesis, in spite of all our science. As they view our feeble attempts to duplicate their sorcery, how the wood-nymphs must laugh!

If we burn plant material, the energy that is released as heat is an exact measure of energy that was stored during the life of the plant, in the process of photosynthesis. Plant products represent stored sunshine. A lump of sugar may be sunshine received last summer by the chloroplasts of beet leaves in Nebraska; a lump of coal, sunshine that fell upon the chloroplasts of tree ferns in Pennsylvania during the Carboniferous Era, millions of years ago.

The total energy emitted by the sun in a year has been estimated to be about equal to that which would be obtained by the burning of 4×10^{23} tons of anthracite coal.* This is about 60 times the mass of the earth. If the earth were made of anthracite coal, its complete combustion would just about supply the energy that is radiated by the sun in six days!

Of this tremendous output of energy, the earth receives but a very small fraction. Yet, so far as we can tell, it

* Abbot, "The Sun," p. 299.

Photosyn-
thesis as a
Means for
Storing
Energy

is the only part of that energy that goes to support life. When we contemplate such an establishment as the sun, operated apparently for the sole benefit of terrestrial life, we wonder whether we are worth it. A large part of the solar energy that does fall on the earth is reflected off into space, or goes to warm the earth's atmosphere. At the surface of the earth, in temperate latitudes, the solar energy received may be around 500 calories per square centimeter of horizontal surface per day, during the spring and summer months. For an acre of the ground, during a growing season of three months, that would be equivalent to the heat released in burning about 250 tons of anthracite coal. Let us compare this with the fuel value of different crops, grown on an acre of land, during a growing season of 90 days, expressed in tons of anthracite coal:*

25 bushels of shelled corn	= 0.33 ton of coal
67.5 gallons of alcohol (fermented from 25 bushels of corn)	= 0.20 ton of coal
75 cubic feet of redwood	= 0.41 ton of coal
89 cubic feet of eucalyptus wood	= 0.83 ton of coal

Yet the sunlight that produced any one of these crops was equivalent to 250 tons of coal! Plainly, only a very small part of the solar energy that falls upon a growing plant is actually used in photosynthesis. Perhaps fifty times that amount is used in evaporating water from the surface of the leaves. The green plant is thus a very inefficient device for storing energy. There is no hope that alcohol can be produced from growing crops in sufficient quantities to meet our needs for liquid fuel, when our supplies of petroleum become exhausted. We shall have to depend on liquid fuels produced from coal, which represents solar energy that was stored during long ages

* Spoehr, "Photosynthesis," p. 33.

of time, before the appearance of man. The present supplies of coal may last several thousand years. That may give us time to discover means for harnessing the solar energy that falls on the waste places of the earth. And the sun may thereafter continue to radiate heat for some millions of years. That may give us time to solve the problem of overpopulation, or put an end to war.

CHAPTER XX

PLANT PRODUCTS

PHOTOSYNTHESIS, complex as it is, is but the beginning of the chemical labors of the plant. Along with the production of carbohydrates, that of nitrogenous substances, the proteins, goes hand in hand. The manifold chemical activities of the plant are, moreover, accomplished with the aid of enzymes—organic catalyzers—which themselves must be created. The plant not only uses chlorophyll, for example, but builds it.

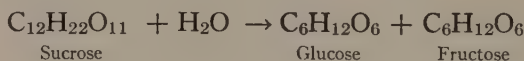
All these substances must be transported from the places where they are synthesized to the places where they are used. In being transported they usually need to be chemically changed. Insoluble substances need to be rendered soluble. Poisonous substances need to be rendered non-poisonous. The plant must choose and select, safeguarding and conserving the useful products of its chemical activities, and discarding or destroying the rest. It must put by stores of nutrient material, in stem, root-stocks, tubers or seeds, to be drawn up in some future emergency, or to support a new generation. It provides bases of supply, and lays down caches of food and fuel, with all the precision of a well-planned polar expedition. We shall presently trace some of these chemical changes that are incident to the plant's business of being alive. By way of preparation, we shall need to disclose a little of what has been discovered about the chemical make-up of the chief products of plant activity.

SUGARS

The earliest organic analyses showed that sugars are compounds containing carbon, hydrogen and oxygen.

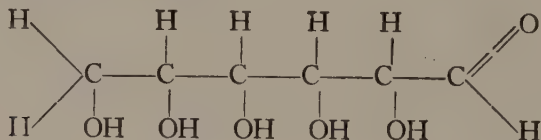
The Simple Sugars Cane sugar, beet sugar and maple sugar, when purified, are chemically identical, with the formula $C_{12}H_{22}O_{11}$. For that matter, milk sugar and malt sugar have that formula, too; but since they differ from cane sugar and from each other in their chemical properties, their atoms must be differently arranged within the molecule, and therefore they have different structural formulas.

The first clue to the structural formula of cane or beet sugar (chemically called *sucrose*) is that a trace of acid, in the presence of water, will quickly convert it into a mixture of two simpler sugars, glucose and fructose. These have the same molecular formula, $C_6H_{12}O_6$, but different structural formulas:



The acid which brings about this change is used simply as a catalyzer. It speeds up the reaction, without being itself permanently altered. The mixture of equal weights of glucose and fructose thus obtained is often called *invert sugar*.

Now let us consider glucose, the most important of the several simple sugars of the formula $C_6H_{12}O_6$. It is easy to show that it contains five hydroxyl groups. **Glucose** If we link up the six carbon atoms to form a chain, and give each one a valence of four, we get the structural formula:



or, $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CHO}$. This formula assumes that the five hydroxyl groups present are connected with five different carbon atoms—an assumption which experience with other compounds renders probable. This formula also assumes that there is a $-\text{CHO}$ group, namely an aldehyde group, at the end of the chain, since glucose has some chemical properties in common with compounds which are known to possess such a group.

Glucose is optically active (p. 91). Thus we need to take account of the different possible modes of arranging its atoms in space. Each of the four inner carbon atoms in the structural formula above is connected with four atoms or groups of atoms that are all different from one another. We have seen (p. 98) that in any such case either a right- or a left-handed arrangement is possible.

Let us represent the four asymmetric carbon atoms of sugar by four men, whom we shall line up in a row from left to right. The first man in the row may be left-handed and the other three right-handed:

L R R R.

Or the first man may be right-handed and the other three left-handed:

R L L L.

The second arrangement is the "optical opposite" of the first. Altogether, there are sixteen different possibilities:

{	L R R R	{	L L L R	{	L R L R	{	L L R L
{	R L L L	{	R R R L	{	R L R L	{	R R L R
{	L L R R	{	L L L L	{	L R R L	{	L R L L
{	R R L L	{	R R R R	{	R L L R	{	R L R R

In listing them we have paired optical opposites together.

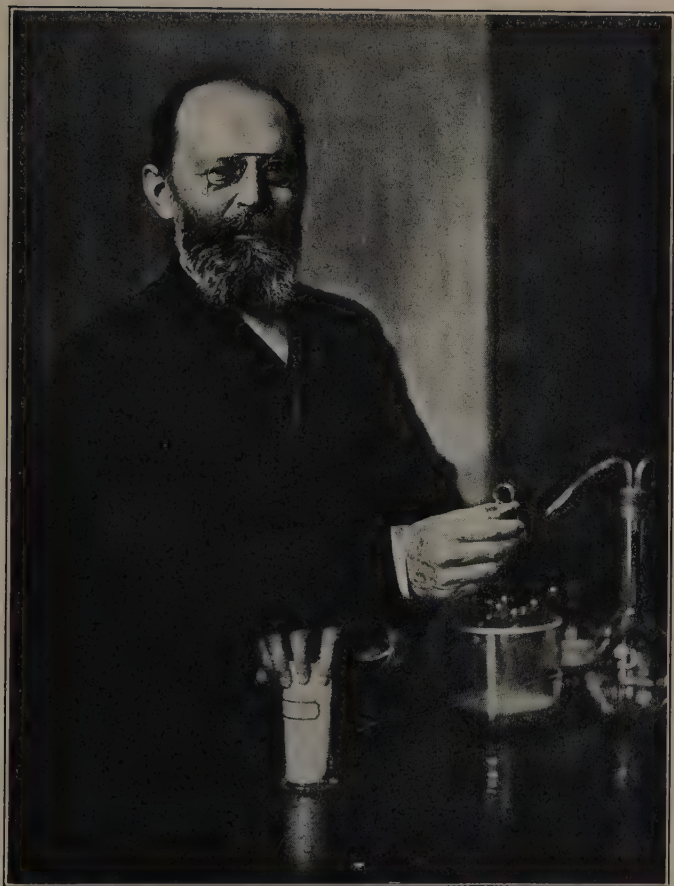
Sixteen
Related
Sugars

By analogy it is easy to see that there must be sixteen sugars, including glucose, of the same structural formula, but differing from each other in their space formulas, according as the atoms and groups attached to the four asymmetric carbon atoms are arranged in a right-handed or left-handed order. These sixteen sugars should fall into eight pairs, the members of each pair being chemically identical, but having equal and opposite effects on polarized light.

All this might have been foreseen as soon as Van't Hoff and Le Bel revealed the architectural possibilities of atoms in space (1875). At that time, however, only four simple sugars of the formula $C_6H_{12}O_6$ were known, and it was not until 1885 that a German chemist, Kiliani, proved that two of these, glucose and galactose, possess the general structural formula which we have assumed above. The other fourteen remained to be discovered.

At this moment the problem of the space formulas of the sugars attracted the attention of the greatest synthetic organic chemist of modern times. This was Emil Fischer, a pupil of Baeyer, the discoverer of synthetic indigo. Fischer had already won fame by researches in which he had prepared many interesting organic derivatives of hydrazine, NH_2NH_2 , a compound analogous to ammonia, NH_3 , in its capacity of combining directly with acids to form salts.

One of these derivatives of hydrazine was *phenylhydrazine*, $C_6H_5NH \cdot NH_2$, in which a phenyl group, C_6H_5 , replaces one of the hydrogen atoms of hydrazine itself. Fischer discovered that phenylhydrazine reacts with the simple sugars to form colorless or yellow crystalline compounds (phenylhydrazones and osazones), of different degrees of solubility and different melting points. Thus with the aid of phenylhydrazine, the different simple sugars in a mixture of sugars might readily be separated and identified. So, by a natural transition, Fischer passed from a study of the derivatives of hydrazine, which had



Courtesy of Rudolf Lesch

EMIL FISCHER

Born in Euskirchen, Phenish Prussia, in 1852. Studied under Kekulé and Baeyer. Worked out the constitution of rosaniline and uric acid derivatives, and many simple sugars. Threw important light on the proteins and tannins. Professor at the University of Berlin from 1892 until his death in 1919.

occupied him for many years, to a study of the sugars themselves—a field in which he immediately won the most brilliant results.

With the aid of the versatile reagent, phenylhydrazine, he next transformed glucose ("grape sugar") into fructose ("fruit sugar"). Thus he revealed the relationship of these two sugars to each other. He then discovered how to cause certain simple compounds, with two or three carbon atoms in a molecule, to "condense" or "polymerize" to form four-carbon or six-carbon compounds. Thus, in 1887, he produced the first purely synthetic sugar, which was later proved to be the inactive (*dl*) form of the natural (left-rotating) sugar fructose.

New triumphs followed in quick succession. Fischer made splendid use of a method devised by Kiliani, whereby the chain of carbon atoms in the simple, six-carbon sugars may be lengthened, one carbon atom at a time, as an engineer lengthens a bridge, span by span. Thus he produced seven-carbon and eight-carbon sugars, quite unknown in nature. Then these new compounds were torn down, atom by atom, to see what sort of simpler products they would give. By a continuation of this same process, glucose has since been degraded, step by step, to a simple two-carbon compound.

Thus by seven years of labor (1887–1894) Fischer not only produced many new sugars but disclosed how they were related to one another, how they might be converted into one another, and how they might be elaborated into more complex products or degraded into simpler products. This latter achievement, in particular, was of the greatest practical importance, as throwing light on the transformations which the fats and sugars (especially glucose) undergo in our own bodies. For every voluntary or involuntary muscular movement is made at the expense of energy that is chiefly derived by oxidizing fats and sugars, to produce simpler compounds of the very sorts that Fischer did so much to make familiar. Of the

sixteen possible sugars of the glucose group, fourteen have thus far been synthesized, and only two remain unknown.

It was long ago observed that a freshly prepared glucose solution rotates polarized light very strongly toward the right; but as time goes by the amount of rotation very slowly decreases, until it has fallen to about half of the original value. The same result is brought about quickly by adding a mere trace of ammonia to the freshly-prepared solution.

Recent
Work on
Glucose

These facts suggested that glucose, like acetoacetic ester (p. 87), exists in two different forms, which are readily convertible into each other:



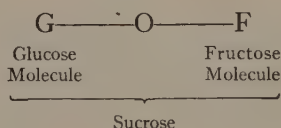
The phenomenon of changing rotation (now called *mutarotation*) would thus be explained by assuming that solid glucose (α -glucose) is in part slowly converted into β -glucose after it has been dissolved in water, until a mixture is produced that rotates the plane of polarized light only about half as much as the original material. The two forms are now known to differ in the manner of linkage of the oxygen atom which has been represented above—somewhat inaccurately—as occurring at the end of the carbon chain.

In relating all this, the story of the complexities of glucose is barely begun. Evidence goes to show that there are probably other forms of glucose than the two we have here mentioned, which are formed from the latter by addition or loss of a molecule of water. Similar complexities probably exist for every one of the sixteen sugars of the glucose group of sugars. Then there is the fructose group of six-carbon sugars, and other groups of sugars with five atoms of carbon in the molecule; and all these present similar opportunities for variations of molec-

ular architecture, through shifts in the order of attachment of H and OH, or in the manner of linkage of oxygen. No wonder it has been remarked that if we still retain the name "simple sugars" to refer to glucose and its relatives, this is perhaps in an ironical sense! It is typical of the complexity of organic nature that a molecule containing only six carbon atoms, and only twenty-four atoms in all, may continue to treat the world to fresh surprises, more than a century after its discovery.

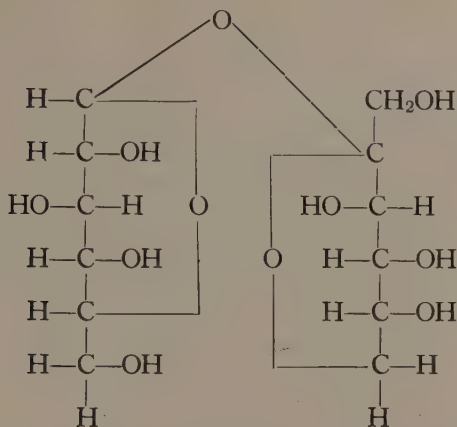
We have seen that a molecule of sucrose (cane or beet sugar) consists of a molecule of glucose, linked in some

Sucrose manner with a molecule of fructose. But how? The fact that the linkage is readily broken under the influence of dilute acids suggests that an oxygen atom, rather than a carbon atom, may be the connecting link:



But is this connecting atom of oxygen one of those in the glucose molecule, or one of those in the fructose molecule? Which one, in either case? The answer was revealed by the British chemist, Irvine, in 1923. His method, briefly indicated, was so to treat sucrose as to get rid of all its hydroxyl groups, replacing them by methoxyl groups, ---OCH_3 . The substance thus obtained was then split up, under the influence of acids, yielding products whose structural formulas, when these were finally worked out, revealed two new hydroxyl groups (one in each molecule), derived from the oxygen link. By locating these newly created hydroxyl groups, the manner of connection of the glucose and fructose parts of the molecule of sucrose was revealed. After a century and a half of continuous observation and two generations of the most intensive research, beginning with the labors

of Kiliani, the structural formula of sucrose was at last disclosed:



This, then, is what we put into our sugar bowls! Why it should be sweet puzzles us still. The structural formula just given doubtless displays the answer, but we do not yet know how to read it.

STARCH AND CELLULOSE

By the method that has just been described, Irvine and his associates have gained an insight into the structure of several other complex carbohydrates. Glycogen, an insoluble white powder that occurs in the liver of animals, has been found to consist of glucose molecules, linked in a peculiar way. Inulin, a starch-like body found in the Jerusalem artichoke, consists of fructose molecules, connected in a manner that has now been established. Starch itself is produced by a linkage of glucose molecules according to a plan that is slowly being unraveled. These researches have already led to some interesting new syntheses, for example the synthesis of milk sugar, chemically called lactose (1927), by combining glucose with another six-carbon sugar, termed galactose.

The new methods have been applied in attempts to determine the structure of cellulose. The cellulose molecule has been shown to consist of glucose molecules, linked together through oxygen atoms that have been definitely identified. Whether the final structure is a chain or a ring has been an open question. But cellulose, when examined with X-rays, proves to possess a crystalline structure, with atoms regularly spaced; and evidence published in 1926 and subsequently, shows that the cellulose fibre probably consists of chains of linked glucose molecules, laid down side by side, like chains of beads, to form a regular pattern.

This is all very plainly of the greatest practical importance in researches that have to do with the mechanical strength of cellulose products, such as rayon and lacquers. Should future research produce rayon that is able to maintain its strength in wet weather, or lacquers more permanently brilliant than those in use today, we shall probably trace these discoveries to the highly academic labors of the chemists who spent many years in revealing the hidden linkages within the cellulose molecule, and to theoretical physical researches designed to reveal the arrangement of atoms within crystals.

The reader will now understand how very complex some of the most familiar substances are. Chemists are at work wresting Nature's secrets from her one by one. Yet she guards them well. Decades of labor on the part of the best minds and most skilled hands of the chemical profession are often needed to disclose a single structural formula. And there are thousands of important substances in nature with structural formulas still unknown.

However, at last we have the satisfaction of being able to set down letters on a printed page, link them together by straight lines, and say that we have made a plan of the structure in space of a molecule of sucrose or cellulose.

**Synthetic
Sugar and
Cotton?**

These structural formulas, no doubt, will some day lead to the synthesis of sucrose and cellulose. Yet that too will call for years of labor, and the methods of synthesis will need to be very different from any known today if they are to stand any chance of competing with Nature's methods. Humanity consumes each year some 28 million tons of cane and beet sugar and some 8 million tons of cotton, all produced by photosynthesis, in green leaves. Not one molecule of either substance has ever come into being through synthesis from carbon dioxide and water, by human efforts. The chemist of today may only point to his services in purifying these materials or in developing uses for their derivatives.

PROTEINS

Complex as the carbohydrates are, they are simplicity in comparison with the *proteins*, the principal nitrogenous constituents of living matter. Egg albumin, the glutinous part of cereals and the lean tissues of meat are protein materials. Hair, horn and gelatin are albuminoids, a group of substances closely related to the true proteins. Proteins contain carbon, hydrogen, nitrogen and a small amount of sulfur. The nucleo-proteins, which are the chief constituents of egg yolk, nervous tissue and the nuclei of living cells in general, contain the four usual elements of proteins, with phosphorus in addition. There are other substances, closely related to the proteins, which contain iron or other elements.

In the tissues of plants and animals, the proteins are of course intermingled with all sorts of material of non-protein nature. Even if these impurities are removed—the fats, for example, by extraction with ether or some other fat solvent—the protein residue is found to

Proteins

Separation of Proteins

be a very complex mixture. Gluten, the protein part of wheat flour, may be separated from starch by kneading the flour under water. The sticky mass that is thus obtained contains at least two distinct proteins. The alcohol-soluble proteins may be removed by extraction with alcohol. Then extraction with a solution of common salt will remove others still. Such methods, however, do not give any very complete separation of the protein products from each other. In favorable cases a fair separation is attained by repeated fractional precipitation by the addition of an ammonium salt, followed by a process of dialysis * to remove impurities, and perhaps in the end by a slow evaporation leading to crystallization; for the proteins, in spite of their complex nature are nevertheless sometimes crystallizable.

In 1820 it was discovered that when gelatin or glue is boiled with acids it is decomposed into soluble products, among which a crystalline acid, since
 Amino Acids named *glycine*, has been identified. Glycine is aminoacetic acid, namely acetic acid in which a hydrogen atom has been replaced by an amino group, NH_2 .



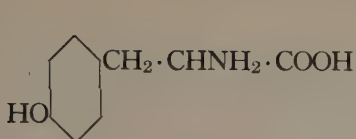
Acetic acid



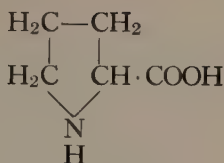
Glycine

Since the discovery of glycine, other amino acids have been recognized. At present about thirty are known. All of these may be regarded as derived from simple nitrogen-free organic acids, by replacing one or more hydrogen atoms by amino groups or by other nitrogen-containing groups. Sometimes the compounds thus produced contain rings of atoms.

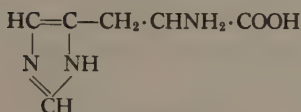
* *Dialysis*, a process of purifying colloidal dispersions, by placing them in contact with a membrane, through which crystalline impurities pass outward and are removed.



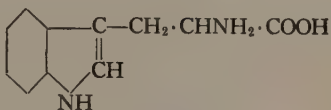
Tyrosine



Proline



Histidine



Tryptophane

Investigators long ago made plain that protein molecules are constructed by linking amino acid molecules together, but the problem of determining the structure of any particular protein, such as the chief constituent of egg albumin, proved very difficult. If the protein material was resolved into its constituent amino acids by being boiled with hydrochloric acid, a mixture of amino acids was obtained. These proved to be very difficult to separate from each other. Very little progress was made until Emil Fischer, who had just completed his brilliant work on the carbohydrates, directed his attention to the proteins, and developed a method for separating the amino acids from each other.

In principle, Fischer's method consisted in causing amino acids to combine with alcohol to form esters (p. 112), some of which are slightly volatile, and may therefore be separated from each other by fractional distillation in a vacuum. As a result of Fischer's work and that of numerous investigators who have supplemented and further developed his methods, the amino acids that are present in the most important proteins have been identified, and their proportion roughly determined. It turns out that proteins which are very much alike in their physical properties, such as solubility and colloidal characteristics are often chemically quite different. There are

probably still other amino acids to be discovered, and in many instances not over 60 per cent of the original protein material has been accounted for among the products of its decomposition by acids.

Fischer next turned his attention to the converse problem—that of combining the amino acids with each other to form more and more complex compounds, in an effort to synthesize the proteins themselves. He concluded that amino acid molecules are linked together, in forming protein molecules, by a reaction in which the carboxyl group, —COOH , of one molecule connects with an amino group, —NH_2 , of another molecule, to form a —CO—NH— group.

Fischer synthesized a number of compounds, which he named polypeptids, that contained two or more amino acid molecules, linked together in this way. These products were in some instances identical with those produced by the incomplete resolution of proteins by the action of very dilute acids. Thus the —CO—NH— linkage does actually exist in the molecules of the proteins themselves. The proof of this was an important step in efforts directed toward the synthesis of the proteins.

In 1907, by tedious, round-about methods, requiring months of effort, Fischer succeeded in linking as many as eighteen amino acid molecules together, to produce a compound with a molecular weight of 1213. In 1916 his pupil, Emil Abderhalden, linked nineteen amino acid molecules together, to produce a compound with a molecular weight of 1326. These are probably the most elaborate molecules of known structural formula that have ever been produced by human synthesis. They cost years of effort. Yet they were not proteins. They proved to be non-crystalline substances, soluble with difficulty in hot water, and possessed many of the properties of proteins; but the natural proteins are of more complex structure still, and doubtless possess several other types of linkage, joining amino acid molecules together, in addition

to the —CO—NH— linkage that Fischer employed. Egg albumin, which is known to be one of the simplest proteins, has a molecular weight of about 34,000!

Many other important investigations in the field of the proteins have been carried out during the past generation by Abderhalden and his students, who have published several hundred papers, dealing with the physical properties and colloidal behavior of many different proteins and albuminoids, and with the elaboration of new types of compounds, leading toward the synthesis of the proteins themselves. Meanwhile Thomas B. Osborne, with his students, at Yale University, made thorough studies of the proteins that are produced by different species of plants, particularly the cereal grains. Other investigators by the score have undertaken work that relates to the physical properties of the proteins, considered as colloidal structures, such as their behavior in the presence of dilute acids, alkalies, and salts. Work of this sort is constantly becoming more important in the progress that is being made in mastering Nature's handiwork in this part of the Realm of Carbon.

There seems little doubt that the proteins will eventually be synthesized. Yet man's synthetic efforts by present methods, extending over many months, yield compounds that are very much simpler than those which a living plant is able to synthesize in a few minutes. If we are ever to produce synthetic food, it will first be synthetic fats, or perhaps synthetic carbohydrates. The proteins are apt to elude us for a much longer time.

The proteins are not only extremely complex but amazingly varied. And no wonder. There are over thirty different amino acids, serving as units in the elaboration of the proteins. These are linked together in various orders and by various types of linkage, to build a new structure containing hundreds or perhaps thousands of such units. The number of different arrangements of the structural units

Recent
Progress

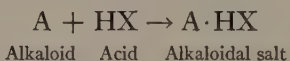
Infinite
Variability

that is thus made possible is of the order of the number of inches to the nearest fixed star. It is not so remarkable that each species of plant or animal produces its own characteristic proteins. The marvel is that Nature ever produces two protein molecules of the same kind.

Yet in the chromosomes of each germ cell there exists something that controls not only the bodily form and function of descendants in succeeding generations, but the minutest details of structure of multitudes of different sorts of complex molecules, including those of the proteins that are characteristic of the species. It is as if the plans and specifications of a great city were to be compassed within a few points just visible to the microscope. Yet living matter in the long course of evolution still continues to unfold new complexities; while non-living matter ever drifts down hill toward more complete disorganization.

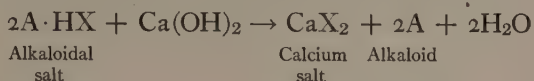
The proteins and amino acids are the most important nitrogenous constituents of plants, but by no means the only ones. In 1806 a German pharmacist obtained from opium a crystalline substance which he named morphine. Its interesting properties led to a search for other substances of the same type, which were soon found in numbers in practically every order of the plant kingdom. At present the great group of *alkaloids*, to which morphine belongs, includes above two hundred members. Opium, the dried juice of the Oriental poppy, contains more than twenty.

The most striking property of the alkaloids, familiarly called "organic bases" is their capacity for combining directly with acids to form salts:



It is the alkaloidal salts, that is, the alkaloids in combination with organic acids, which are found in plants. To

separate the free alkaloid, the plant material is commonly dried, finely ground, and boiled with limewater:



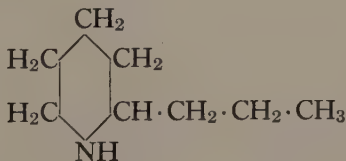
Then, by extracting the water solution with an organic solvent, such as ether or chloroform, the free alkaloid may be obtained.

As other alkaloids were discovered one by one, during the century that followed the discovery of morphine, workers sought to unravel their structural formulas. The methods were those illustrated by camphor (p. 83):

(1) *Distillation in the presence of dehydrating agents*, which generally produced simple derivatives of pyridine and quinoline, and thus revealed the presence in the alkaloids themselves of the pyridine and quinoline rings (p. 70).

(2) *Regulated oxidation*, which stripped off the substituting groups or chains of atoms attached to these rings, and left carboxyl groups $-\text{COOH}$, in their stead (p. 82). The problem was thus reduced to one of upholstering the rings at specified positions with groups to correspond with the composition and properties of the original alkaloids.

It turned out that some of the alkaloids are of very simple structure. Conine, for example, one of the six alkaloids present in poison hemlock, responsible for the death of Socrates, is merely:



Such a simple compound was of course synthesized very early.

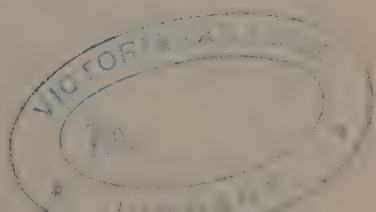
Cocaine and its synthetic substitutes have already been mentioned (p. 158). Other natural alkaloids are still more complex, and many of them, including some of the longest known and most important members of the group, such as morphine, strychnine, and quinine, have not yet been synthesized.

CHAPTER XXI

PLANT ACTIVITIES

THE numerous classes of organic substances that are produced by plants serve many different purposes. In many instances we know what these purposes are, but in others we do not. The chemical activities of plants have been much less completely studied than those of animals, yet the information that we have seems to indicate that many of them follow the same general directions. The carbohydrates, fats, and proteins, for example, are transported from one place to another within the organism by being resolved into simpler, soluble substances, in plants and animals alike. When these products are oxidized, to release energy for the vital activities, the intermediate products of oxidation, leading to water and carbon dioxide, have often been detected in both the plant and animal economy. It is quite possible that the enzymes by which these changes are accomplished are often identical in both types of organization.

In considering the chemical activities of plants, let us begin with the plant acids. Many of these were discovered by Scheele, a century and a half ago. Nettles produce formic acid; citrus fruits, citric acid; apples, malic acid; and so forth. We do not know why different plants should produce different acids nor just what purposes acids serve in the life of plants. It is probable that they play a part in insuring that the enzymes which accomplish the conversion and reconversion of carbohydrates, fats and proteins are assured of surroundings of the degree



of acidity in which they happen to operate best. The organic acids, by combining with alcohol, produce esters, that make fruits and seeds or tubers more attractive food for animals and man. Thus they aid in securing a wider distribution of plants because of the scattering of seeds by animals.

The soluble carbohydrates (sugars) produced by photosynthesis are transported to all parts of the plant, and are there oxidized to furnish the local needs of the plant for energy. When energy needs to be stored for future growth, or for the development of seeds, a considerable reserve supply of soluble or insoluble carbohydrates may be laid up in some particular part of the plant. If the plant needs to withstand freezing, it usually stores a reserve supply of soluble carbohydrate (a sugar), since a solution is thus obtained that has a much lower freezing point than pure water. Otherwise it usually stores an insoluble carbohydrate (starch or, occasionally, inulin). Starch is readily identified by the fact that it is stained blue by iodine and is hydrolyzed by dilute acids to form glucose. Inulin, which is a white solid, resembling starch, is not stained by iodine, and is hydrolyzed by dilute acids to form fructose. It is found in the tubers of dahlias and Jerusalem artichokes.

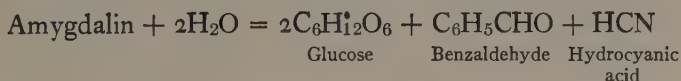
Aside from the use of carbohydrates as a source of energy and as a reserve supply of plant food, we find cellulose in the cell walls of annual plants and in the younger parts of trees and shrubs. As these parts grow older the cellulose combines with lignin, a material of unknown composition, and is thus converted into wood. Finally, in the pithy part of corn stalks, in corn cobs, and in many seeds we meet with a group of insoluble carbohydrates called pentosans. These differ from cellulose in being non-fibrous, and in forming sugars of the formula $C_5H_{10}O_5$, when hydrolyzed by dilute acids.

The sugars, especially glucose, are able to combine with

a great many other substances—alcohols, aldehydes, phenols, organic acids, hydrogen cyanide, and pigments—to form compounds called glucosides. Hundreds of these are known, of the most diverse compositions. They can be obtained from the most widely varied sorts of plants, by first heating the plant tissues to destroy enzymes, and then extracting them with hot water or alcohol. It appears that the glucosides are localized in certain plant cells, while neighboring cells contain enzymes that are capable of resolving them into sugar plus non-sugar. If the plant material is ground and extracted without the preliminary heating, the enzymes decompose the glucoside.

Glucosides stock the medicine chest of the plant. If a plant is wounded or bruised, the breaking of the cell walls permits the enzymes to act upon the glucosides, and antiseptic or germicidal substances, such as phenols or hydrocyanic acid, are set free. Thus bacteria and fungi are restrained, which would otherwise find an ideal culture medium in the fluids that fill the plant cells. Races and strains of plants which are resistant to bacterial and fungus diseases perhaps often owe their resistance to a better protection by glucosides. It is thought that the substances set free when glucosides are decomposed by enzymes may often act as stimulants to growth, or hasten the repair of bruised or wounded tissues.

One of the most famous glucosides is *amygdalin*, which was one of the first substances of this group to be recognized and studied (1830). It is found in the kernels of bitter almonds, apricots, peaches and plums; in apple seeds; and in fact in the seeds of practically all the plants of the rose family. It is accompanied, in neighboring cells, by the enzyme *amygdalase*, which can decompose it into glucose, benzaldehyde, and hydrocyanic acid.



A number of other glucosides are known that yield hydrocyanic acid on being decomposed by enzymes. Plant material containing them—some wild varieties of beans or cassava for example—may be violently poisonous if eaten without a preliminary treatment, designed to decompose the glucoside and get rid of the hydrocyanic acid.

Another famous glucoside is *indican*, which is found in the indigo plant. When this is decomposed by its appropriate enzyme, it yields glucose and a colorless compound which is readily oxidized by the air to an insoluble blue dye, indigo. It is interesting to notice that the red, yellow, blue and violet pigments of fruits, flowers and leaves are either glucosides, or are derived from glucosides by simple chemical changes.

The tannins are phenol-acids, or glucosides containing phenol-acids. They may be extracted from many different barks and roots, and have been used

Tannins

since ancient times for altering hides into leather. This they do by combining with some of the proteins of the hide to produce material which is more resistant to the attacks of micro-organisms, and which does not swell so much when placed in water. The bitter or astringent taste of unripe fruits is due to tannins, which are converted into other compounds as the fruit ripens, or are rendered tasteless by being surrounded by insoluble and impermeable cell walls.

The edible fats and oils produced by plants are apt to be concentrated in the seeds, in order to supply

reserve material to the seedling plant in the first stages of its growth. The chemical changes by which fats are made available as sources of energy are undoubtedly begun by a resolution of the fat into a mixture of glycerol and fatty acids (p. 217). Yet plants possess the ability to convert fats into carbohydrates, proceeding by way of glycerol and fatty acids; and conversely, to convert carbohydrates into fats. Transformations of this sort have been accomplished in

the chemical laboratory, but only with great difficulty, and by means that are incomparably more labored than those employed by living organisms. The methods by which plants and animals pass so freely from the carbohydrate state to the fatty state are quite largely mysteries to us still, in spite of all our skill in synthesis.

The lipid substances are intermediate in their chemical nature and physical properties between the water-soluble sugars and the water-insoluble fats.

Lipoids

They absorb and hold large quantities of water without dissolving, and are thus of particular importance in the plant or animal economy, as reservoirs of moisture. Lipoids in general are fat-like substances, in which one of the three fatty acid radicals present in ordinary fats, combined with glycerol, is phosphoric acid, in combination with a nitrogenous organic base, such as *choline*, $C_5H_{15}O_2N$.

Lipoids are universally present in living plant and animal tissues, in the nuclei of cells and in the parts of the living organism in which the vital phenomena are most pronounced—in animals, for example, in the brain, spinal cord, and nervous tissue. They are intimately connected with life, but we are not yet sure just what part they play. They are much more readily alterable chemically than the proteins and fats, and are sometimes viewed as being useful in the chemical mechanism by which the fats and proteins are synthesized.

The essential oils, such as turpentine and cedarwood oil, are very different in chemical composition from the edible fats and oils. In general, they are

Essential Oils

hydrocarbons. They are so very diverse in their chemical natures as to suggest that they serve very different ends. Some of them doubtless have antiseptic qualities, which help to preserve the living plants against the attacks of micro-organisms. Others may be simply waste products, that accumulate as incidents to the other chemical activities of the plant. Rubber is

a plant hydrocarbon. Though it is of great industrial importance, we do not understand why plants produce it, nor why they produce turpentine.

Proteins are synthesized in the plant by chemical changes which are not directly the result of photosynthesis. If the proper supply of inorganic nitrogen and sulfur compounds are present, together with carbohydrate to serve as a supply for carbon and energy, proteins may be synthesized in the dark. Nevertheless, the synthesis of proteins is usually carried on in the leaves, jointly with the formation of carbohydrates by photosynthesis. In general, the nitrogen that is used in the construction of the proteins must be furnished to the plant as an inorganic nitrate, and the sulfur as a sulfate, though many plants can absorb these two elements in other forms.

We know nothing of the way in which the nitrogen or sulfur is sometimes built into ring compounds. It is apparent, however, that the plants can construct complicated ring structures in a much more ready fashion than we can do this in the laboratory. The methods in which powerful reagents, such as nitric acid, sulfuric acid, chlorine and caustic potash are brought to bear in effecting artificial syntheses of the ring compounds that are of importance as dyestuffs or medicinals are vastly different from the ready elaboration of these same groups of materials by plants.

The elaboration of proteins by plants doubtless begins with amino acids and runs up through products that are more and more complex, until true proteins are finally reached. Conversely, when protein material is moved or translocated from one part of the living plant to another, it is first resolved into amino acids, which are transported and then resynthesized. These processes, too, are still almost complete mysteries to us.

The pectins are colloidal carbohydrates that thicken the cell walls of certain plant tissues or are present as

cementing material between adjacent cells. Apples and the rind of citrus fruits are especially rich in pectic substances. In the cell walls of plants or in the middle lamella between adjacent cells the pectins are insoluble in water, and perhaps often exist in combination with cellulose. In this condition they are called *protopectins*. By heating with water under pressure or by the action of enzymes they are converted into soluble pectins, which form viscous solutions.

The pectin of commerce is usually extracted by heating apples (or other fruits rich in pectin) with water under pressure, or by digesting the finely pulped material with a five-tenths per cent solution of ammonium oxalate. It is used in the preparation of jellies and jams, to cause the juices of fruits to gel that are deficient in pectin. Delicately flavored material is thus spared the long boiling that would otherwise be necessary to concentrate the solution sufficiently to enable it to gel on being cooled.

The ripening of fruit is accompanied by a transformation of the insoluble protopectins of the middle lamella, between adjacent cells, into soluble pectins. This results in the weakening or collapse of the whole structure, much as a building would be weakened by the removal of the mortar between adjacent bricks. We then say that the fruit has become mellow. The micro-organisms responsible for rots and blights of cultivated plants are believed to penetrate the plant tissue by secreting an enzyme that dissolves the cementing layer of protopectin, between adjacent cells. A slimy disintegration of the plant tissue ensues.

In spite of extended research, the structural formulas of the pectins remain undetermined. We only know that soluble pectin is a methyl ester of a complex acid, pectic acid, the alkali salts of which may be prepared by treating soluble pectin with dilute alkalis. Pectic acid is known to be formed by linking together several molecules of galacturonic acid, $C_6H_{10}O_7$, through oxygen atoms.

Roughly stated, galacturonic acid is to pectic acid as glucose is to starch or cellulose.

For each of the types of chemical transformation that we have just mentioned, there is present in the plant an enzyme or group of enzymes that appears to be specially adapted to effecting it. The **Enzymes** as a class are perhaps related to the proteins. Their isolation in pure form is made difficult by the fact that they are present only in minute quantities, in admixture with many other materials. We can only follow them through the processes that are used to purify them by taking note of the catalytic activity of the successive products that we obtain; yet if we go too far in the process of purification we often find that the catalytic activity disappears altogether. This leads to the assumption that many enzymes need to be activated by the presence of other substances, such as traces of manganese salts.

So far as we know, the enzymes are specific in their action. That is, each enzyme is designed to induce a particular kind of chemical change. Those responsible for the conversion of starch into maltose and glucose are collectively known as *amylases*. Those that transform fats into glycerol and fatty acids are called *lipases*. Those that are responsible for certain processes of oxidation that go on in plants are called *oxydases*. Those that decompose hydrogen peroxide into water and oxygen are called *catalases*.

We do not know whether enzymes that accomplish the same chemical action but that appear to be different in their rate of action or the conditions under which they act are really different, or whether the differences in their behavior are caused by differences in the nature of the substances that accompany them. The entire field relating to the nature of enzymes and the manner in which they work is enshrouded in mystery, in spite of numerous detailed investigations. It is a branch of organic synthesis in which the plants possess secrets all their own.

CHAPTER XXII

THE ANIMAL LABORATORY

THE nature of the changes that occur in the digestion of food by animals was the subject of the wildest speculations during all the centuries that preceded Spallanzani the development of organic chemistry.

Some of the earliest experiments that are recorded in an attempt to determine just what happens when food is digested were those of the Italian naturalist, Spallanzani, about 1780. Spallanzani attached sponges to strings, and fed them to hungry birds of prey; then presently withdrew them and showed that the fluids which they had imbibed during the period in the birds' stomachs were able to digest and disintegrate small particles of food. He also placed bits of food in perforated capsules which were permitted to pass through the digestive canals of men or animals. The food was completely digested by the fluids that penetrated the capsules. This experiment showed plainly that digestion is not accomplished by mechanical grinding, as had previously been surmised, but by chemical action.

About half a century later, evidence concerning the nature of the digestive processes was obtained by observations on a man who had met with a gun-shot wound that made it possible to watch the action of the interior of his stomach during digestion. The rhythmic movements of the stomach muscles were observed, which begin immediately when food is swallowed or even smelled. Later many experiments were performed on animals. In recent years X-ray cinematograph photographs have been

produced, showing the mechanical movements that accompany the digestion of food in the stomach and intestines.

The chief chemical facts concerning the purpose and ultimate fate of food in the processes of digestion were slowly accumulated during the rise of organic chemistry as a science. The work of Liebig had a great deal to do with the classification that was made of foods into two groups: the tissue-building foods, including the proteins; and the energy-supplying foods, including especially the carbohydrates and fats—though the proteins also of course yield energy when they are oxidized in the body.

In addition to supplying the body's needs for new tissue and energy, foods have also to supply inorganic and organic materials of all sorts that serve as stimulants or regulators of the vital processes. For example, salts of sodium, potassium and calcium need to be present in the blood stream in a proper proportion to each other, if the heart is to function properly. In fact, a living heart that is placed in a solution of these salts of suitable composition, in the presence of about one per cent glucose, will continue to beat for a long time outside the body.

Complex organic compounds containing nitrogen, phosphorus, iodine, iron, and very possibly traces of some other elements such as copper and titanium, need to be synthesized in the body, and the food must furnish all these inorganic elements, and must provide them in sufficient supply. When we consider how complicated are the body's needs for food, and how little we have known about them, we may wonder that food selected without any better guide than appetite ever proves to be a satisfactory diet.

In general we find that the transformations that food undergoes in the processes of digestion in animals are roughly of the same sorts as the transformations of the same materials in plants. For example, sucrose as a human food is

The Purposes
of Food

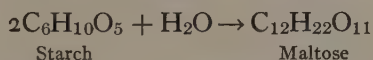
Digestion
of Sugars

inverted or changed into glucose and fructose by the hydrochloric acid that is secreted by the stomach walls, and then the change is completed by the enzyme, invertase, that is secreted by the intestinal glands. This is precisely the chemical change that is induced by the enzyme, zymase, which is contained in yeast (p. 263).

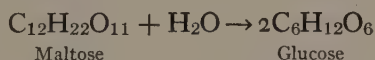
Milk sugar, too, is acted upon by the hydrochloric acid of the stomach walls, and by enzymes secreted by the intestinal glands, producing the two simple sugars glucose and galactose. The latter, in combination with nitrogenous compounds, is a constituent of the brain and nervous tissue. We have in this fact a sufficient reason why it is impossible to replace milk sugar by cane sugar in the nutrition of young animals.

The digestion of starch follows the lines of the decomposition of starch by acids or by the diastatic enzymes of plants. Its digestion is usually begun by the enzyme, ptyalin, of the saliva, forming malt sugar or maltose:

Digestion
of Starch



This action is limited to the upper part of the stomach, where the contents of the stomach have a slightly alkaline reaction, due to the faint alkalinity of the saliva. In the lower part of the stomach, where hydrochloric acid is secreted, the action of the ptyalin is promptly arrested. Then, when the food passes into the small intestine, the maltose is acted upon by the intestinal juices and converted into glucose.



Thus, whether the carbohydrate of our food is sucrose, maltose, lactose or starch, the chief final product of the action of the digestive enzymes is glucose. This is absorbed through the stomach walls and enters the blood stream directly,

Glucose in
the Blood

together with fructose and galactose. The blood normally contains about one-tenth of one per cent of glucose. Elaborate arrangements exist within the body for controlling the glucose content of the blood within narrow bounds. If it falls too low, through lack of proper regulation or through lack of proper food, the animal dies. If it goes too high, for any reason, the result is no less fatal.

Under normal conditions, any excess of glucose entering the blood stream, beyond the body's immediate needs for energy, is transformed into a white, insoluble substance, called glycogen, which resembles starch in its general appearance, and is stored up in the muscular tissues of the body and in the liver. When the body has laid by a good supply of glycogen, any further excess of glucose is converted into fat, which is laid away in any convenient place.

The glucose in the blood supplies most of the body's needs for energy. It is oxidized with the aid of oxygen in the arterial blood in all parts of the body forming carbon dioxide, which enters the venous blood and is exhaled through the lungs. Numerous experiments with animals and men have demonstrated that the quantity of energy which is released by the oxidation of glucose, or indeed of any other material in the body, is precisely the same as if the oxidation took place by combustion in the open air, or in a closed bomb in an atmosphere of oxygen. If there is any sudden demand for energy, glucose is oxidized very rapidly, and immediately replaced from the supply of glycogen in the liver and muscles.

The energy requirements of the body are of course dependent on the amount of work that is done. A man of average weight, lying at complete rest, without even undertaking the labor of digesting food will require about 85,000 small calories an hour. This represents energy that is

Energy from
Glucose

Energy
Requirements

expended within the body in the work of respiration, circulation, and other vital activities, and energy radiated from the body as heat. If the man stands on his feet, the rate of expenditure of energy may be increased by 20 per cent or more. If he undertakes severe exercise it will be increased several fold.

In determining the amount of food that one must take in order to obtain sufficient energy for the work to be done, one does not need to consider whether the calories come from fat or carbohydrates, or, within limits, even from proteins; though it is worth remembering that fats, weight for weight, furnish about $2\frac{1}{4}$ times as much energy as carbohydrates or proteins.

In the digestion and absorption of fatty foods, the first action that occurs is the breaking up of the fat into minute droplets by the vigorous churning action of the lower end of the stomach.

**Digestion
of Fats**

The emulsion thus produced passes to the small intestine, where it is acted upon by the enzyme lipase, which transforms the fat or oil into glycerol and a fatty acid. These are the very products that result when the digestible fats and oils are chemically altered by microorganisms or by the higher plants.

The glycerol and fatty acids pass through the stomach wall and are immediately resynthesized into fat, which may be the same sort of fat that was originally present in the food. If large quantities of fatty foods are digested, the body will not have time to undertake extensive chemical alterations of the fatty acid molecules, and the foodstuff fat will be laid down as such in the usual places of deposition of fat about the body. Cattle or hogs fed on foods rich in cotton seed oil build up fatty tissue which exhibits the chemical characteristics of cotton seed oil. At some later time this material may be worked over to produce normal fat.

The digestion of the proteins begins in the stomach, where they are acted upon by an enzyme, pepsin, which

is secreted by the stomach walls. The stomach walls secrete the proper quantity of hydrochloric acid to activate the pepsin, for pepsin acts only in the presence of acid. Before the digestion of the proteins is complete, the food passes from the stomach into the small intestine, where the bile and pancreatic juices act upon it. Here the reaction is changed from acid to alkaline. A new set of enzymes (trypsin, pancreatin, etc.) act upon the incompletely digested material. The final products are amino acids, which are absorbed directly through the stomach walls and reelaborated in the body to form bodily proteins.

Digestion of the Proteins

The preceding brief survey indicates that the synthetic activities of animals are rather less intricate than those of plants. Plants start with water, carbon dioxide and a few simple inorganic salts, and from these produce the most varied types of compounds: cellulose, starch, sugars, fats, proteins, hydrocarbons, acids, esters, alkaloids, tannins, glucosides, coloring matters, waxes, resins, chlorophyll and enzymes. Animals take possession of carbohydrates, fats and proteins, ready-made. These they resolve into products just one stage simpler, which they then rebuild into the animal mechanism.

Second-hand Building Material

The elaborate molecular structure of hemoglobin, the oxygen-bearing red pigment of the blood, needs to be made, or at least is most readily made, from simpler organic iron compounds produced by plants. Animals apparently do not attempt many synthetic activities that are habitually carried on—and that may just as well be accomplished—by the plants that serve the animals as food. Animals get their most important tissue-building materials second-hand; or third- or fourth-hand, from other animals, which in turn depend on plants. They seem to be unable to synthesize even the small traces of vitamins (save vitamin D and perhaps vitamin C) re-

quired for normal growth and activity. If we include milk, meat, or eggs in our diet, with the thought of adding vitamins, we are making use of material which happened to be stored up in these animal products, but which was really produced by plants on which the animals fed.

Nevertheless, the chemical activities of animals are complicated enough. The materials supplied by food need to be worked over to select the proper ones to be elaborated into chemical products of the most diverse kinds. Each organ in the animal body needs to be maintained in a definite chemical environment by substances brought to it in the blood stream. And since the animal is unable to obtain energy directly from the sun's rays, it must tear down and oxidize material in every part of the body, to obtain the energy that is needed to synthesize other material. Waste products thus arise, which must be eliminated, and protective measures must be set up against the attacks of micro-organisms. All of these chemical activities are under the control of enzymes, which the animal must synthesize or derive, ready-made, from plants. The same is true of the vitamins. Then there are numerous special substances, such as the hormones, to be described in our next chapter, which must be synthesized in minute quantities in order to keep the chemical mechanism running.

Much research has been carried on in an endeavor to lay bare the secrets of each of these chemical activities of animals. Each of them might well be made a chapter in itself if we were permitted to make so extended an excursion into the biochemical province of the Realm of Carbon. Next to digestion, the processes of oxidation that result in the liberation of energy have been made the subject of the most extended investigations. With respect to these, we shall merely remark that all of the oxidizable and reducible substances in the body are in a state of delicate balance with respect to one another. If the body needs to synthesize a substance that is to be built only by

the expenditure of energy or by the addition of hydrogen to a substance already present, then energy or hydrogen will be withdrawn from any substance that can be made to part with it. Such studies have lately given a clue to the manner in which amino acids are synthesized by the plant or animal mechanism.

A generation ago, before the work of Fischer had made possible the separation and identification of the

**What Makes
a Complete
Diet?**

amino acids that occur in chemical combination with each other in different sorts of proteins, it was supposed that any one protein would serve the needs of the body for nitrogen as well as any other. Protein was protein and that was all there seemed to be to it. If a person received enough calories each day in the form of carbohydrates and fats, and enough nitrogen in the form of protein, he was supposed to be sufficiently nourished. The fact that thousands of individuals received food in quantities and proportions that satisfied these requirements and yet suffered from serious derangements, apparently of dietary origin, was not considered significant.

This point of view is now abandoned. We understand that the body has need for certain amino acids which are not contained in all protein foods. The proteins of peas and beans, for example, are thus deficient. This information has chiefly been won with the help of feeding experiments conducted with small animals, on account of the difficulty and expense of securing large quantities of pure proteins of known amino acid content. The result has been to make the science of foods and feeding much more complex than it was thought to be a generation ago. It is only by good fortune that the essential amino acids are usually all present when we select our foods in the off-hand manner that we do.

VITAMINS

It was long ago observed that the natives in certain parts of the world are subject to peculiar diseases, which affected whole populations. Beriberi, pellagra, and rickets were conspicuous examples. Another disease of baffling origin was scurvy, which was apt to take off the entire crew of any vessel that was a long time at sea with only the sort of provisions that could be carried on long voyages. As time passed it was observed that these diseases were often relieved by a change of diet. Dana, in his "Two Years Before the Mast," relates how lemon juice saved his shipmates from death by scurvy.

Animals, too, often suffered from dietary derangements, when given rations that lacked variety, even though all the known elements for complete nutrition were present. It was found that polyneuritis might be induced in pigeons by feeding them on a diet of polished rice; and that the disease might be prevented or cured by the use of unpolished rice, or by the addition to the diet of an extract of the polishings. It seemed likely that beriberi, a disease very common among the natives of Oriental countries that subsisted largely on rice, might be caused by failure to obtain some necessary food constituent, which was removed from the outer portion of the rice grain by the process of polishing.

Extended experiments with animals followed, from about 1907 onward, in which it was demonstrated that a diet containing all the major constituents of food might still be insufficient for normal health and growth. Very often the derangements induced by deficient diets were relieved by a minute quantity of some supplementary material. So little of this was needed that it could hardly serve to supply the body's ordinary needs for building material and energy. It seemed rather to act as a sort of nutritive catalyzer, enabling bodily processes to go

forward that would fail to take place smoothly in its absence, even though all the previously recognized dietary essentials were present in abundance.

These unidentified dietary essentials are now called vitamins. The evidence for their existence is entirely indirect, and is derived from experiments with animals in which restricted diets are supplemented by limited amounts of foods which it is desired to test for the presence of particular vitamins. The problem is complicated by the fact that there are a number of different vitamins, serving different purposes, yet often present together in the same foods, and not readily separable by chemical methods. At present six vitamins are recognized, and it is very probable that others will be found.

Vitamins A, D and E are the fat-soluble vitamins. Vitamin A was discovered by McCollum and Davis, and independently by Osborn and Mendel, in 1913. It was first observed as a growth-stimulant for rats. It seems to be produced by plants in connection with the process of chlorophyll formation, and is plentiful in green leaves, but is accumulated as well in yellow seeds and yellow roots. By including such materials in the rations of dairy cattle, it is possible to increase the amount of vitamin A in butter and milk. This vitamin is readily destroyed by oxidation. Pasteurization therefore usually lowers the vitamin content of milk very appreciably; and cod liver oil, improperly prepared, may be almost valueless.

In 1922 McCollum proved that rickets may be prevented by the use of foods containing small amounts of another unknown dietary essential, now called vitamin D. This is also a growth-promoting vitamin, but its special function seems to be to control the concentration of calcium and phosphorus in the blood, by regulating the absorption and secretion of these elements in the intestinal tract. Thus, indirectly, the vitamin plays an essen-

**Fat-Soluble
Vitamins**

tial part in building structures rich in calcium and phosphorus, such as the bones and nervous tissue.

Several investigators, independently in 1925, made the remarkable discovery that fats and oils from many different sources are enriched in vitamin D, simply by exposing them to ultraviolet light. Later research showed that the vitamin is produced from a substance associated with fats, but is not itself a fat. This has now been identified as ergosterol, an unsaturated solid alcohol, which seems to be present in practically all fats of plant or animal origin in sufficient quantities to enable vitamin D to be produced by exposing the fat to ultraviolet light. The ultraviolet rays of sunlight have proved very effective in preventing and curing rickets; yet the best sources of ultraviolet light surpass sunlight in the rate at which vitamin D is produced. In this respect, synthetic sunlight is an improvement on Nature. It seems likely that the details of the rearrangement of atoms that converts ergosterol into vitamin D will presently be established. The determination of the structural formula of the vitamin and its synthesis from simpler substances may then be expected.

A third fat-soluble vitamin, now called vitamin E, was shown in 1922 to be essential to fertility in the female rat, and is assumed to play a similar rôle with other higher animals. It is widely distributed in foods of plant and animal origin, and is especially plentiful in the oil extracted from the wheat germ. It is remarkably resistant to destruction by heat, light or oxidation, and will even withstand the action of caustic alkalies at moderate temperatures.

The water-soluble vitamins are vitamins B, C and G.

Water-Soluble Vitamins

Observations slowly accumulated during many years led to the belief that the outer portions of the rice grain contain a substance that is removed by polishing the rice and that

gives protection against polyneuritis in pigeons and beri-beri in man. This substance is now called vitamin B. Its chemical identity is still undetermined, though it is known to be a nitrogenous base, perhaps related to pyridine.

Vitamin B is synthesized by yeasts and bacteria, as well as by the higher plants. It is not only a protector against beri-beri but an appetite-stimulant and a growth-promoter; and experiments with rats indicate that it may be of importance in maintaining female fertility. It is destroyed fairly readily by boiling solutions containing it, particularly under neutral or alkaline conditions.

Vitamin C offers protection against scurvy and against some other derangements that appear in its absence, such as certain abnormalities of the bones and teeth. It is primarily a plant product, but may probably also be produced by animals from closely related substances. It is readily destroyed by heating in the presence of air, but fruit and vegetables may be heat-sterilized without destroying the vitamin, if oxygen is excluded. Its chemical nature is still unknown.

Vitamin G is a growth-promoting vitamin of undetermined chemical nature, which is widely distributed in plants in association with vitamin B. It is distinguished from vitamin B by its much greater resistance toward heat and alkalies.

The whole group of vitamins have been well advertised, and promoters of special diets and patent foods have not been slow in putting forward extravagant claims concerning marvelous results to be obtained by the use of their prescriptions. It is necessary to take statements from such prejudiced sources with much reserve. On the other hand, some of the largest and most responsible manufacturers of food products are alert to the importance of the vitamins and are carrying on research that may be expected to furnish important new information on their distribution and chemical nature, and the best means for

preventing them from being destroyed in preserving or cooking foods.



Courtesy of Copper and Brass Research Association

AN EXPERIMENT IN NUTRITION

Most of our knowledge concerning nutrition, especially the need of the body for particular inorganic elements, amino acids and vitamins, has been obtained by experiments with animals. In the experiment shown here, minute traces of copper salts, added to the diet of rats, improved health and stimulated growth.

Thus the matter of setting up a standard diet is a rather complicated problem. We must see to it that the body gets a sufficient supply of energy and protein, perhaps 2500 to 3000 large calories of energy and 75 grams of protein per day, for a man of average weight at light or moderate exercise. Moreover it must be protein of a sort that contains all the essential amino acids.

**Standard
Diets**

In addition, a proper supply of inorganic nutrients, such as phosphorus, calcium, magnesium, sodium, potassium, iron, iodine, fluorine and perhaps other elements must be present. There is particular danger of receiving too little phosphorus, calcium and iron under the conditions of modern civilized life. Feeding experiments with animals indicate that some other elements, such as manganese, or even copper, may need to be present in the food of animals, in extremely small amounts, for normal health and growth. Finally, the vitamins need to be considered, and individual differences between persons that make one man's meat another man's poison. Jack Spratt and his wife had dietary habits that made for economy, but they doubtless came to an early end.

CHAPTER XXIII

CHEMISTRY AND FATE

OUR story of chemistry as related to life has thus far been only the story of how living things—bacteria, plants, or animals—make use of food for building and rebuilding tissue or securing energy. Biology textbooks name this building and rebuilding process *metabolism*. Fortunately that is not all there is to life. If living things merely grew and then wasted away, like frost patterns on a window-pane, they would be no better than crystals. Living things not only build and rebuild, thus maintaining their existence in the face of the agencies of destruction and decay, but they react to external stimuli, and they give rise to other individuals of their own types.

These functions are all matters of chemistry. When a runner makes a hundred yards in ten seconds flat, we witness a chemical prodigy. For the perfect coordination of a hundred moving muscles depends on electrochemical signals flashed and relayed from each nerve center to its neighbors. Every muscular movement causes a chemical alteration of the muscular tissue, which must instantly be readjusted. The sudden call for energy demands that the flameless fire within the lungs must for the moment burn more fiercely.

Nor is there less chemistry in labor of a different sort—say in acquiring an education. The chemical ingredients of the blood bequeathed by one's ancestry have determined whether one takes naturally to exact studies or would do better in a course in appreciation of art. Make

what effort one may, the battle is lost if there are no chemical allies within one's own blood to rise up and prod one through.

HORMONES

Within recent years we have come to know more about the mysterious substances called hormones, which so largely determine what we are and whether we find life worth living. The most important of them appear to be secreted by special glands in different parts of the body. Growth-stimulating substances see to it that we increase in size during childhood, then growth retarders step in and put an end to the process. If we catch the smallpox or measles and survive, our blood has thereby been fortified by chemical substances that make us immune to further attacks of these diseases. Or we may be given an artificial immunity against typhoid or diphtheria by unidentified chemical substances contained in an anti-toxic serum.

Whether we grow to be tall or short, whether we perform motions that are clumsy or graceful, whether we think thoughts that are sublime or foolish, whether we love our fellow men and keep all the commandments from our youth up doubtless depends on the subtle chemistry of the blood and brain. To this we owe the works of creative genius in all the ages, and sex: a world made interesting—and difficult—by the fact that the members of human society are of two very different types. It is by chemical means, again, that the development of the embryo summarizes and reviews the evolution of its race. It is almost as if molecules could remember.

Scattered through the body are a number of "ductless glands," so called because the chemical products that they secrete find no outlet for escape except by entering the blood stream, which carries them to the remotest parts of the body, affecting every organ, including other glands. The duct-

**The Ductless
Glands**

less glands which have been most carefully studied are the adrenal glands, which are associated with the kidneys; the thyroid and parathyroid glands, at the base of the neck; the isles of Langerhans, in the pancreas; the pineal and pituitary glands, below the brain; and the sex glands.

This doubtless does not complete the list. The stomach and upper intestines are known to secrete substances that affect physiological processes in the other parts of the body. Possibly the thymus, spleen, and liver should be included. Hormone secretion, on inconclusive evidence, has even been ascribed to the heart, kidneys, and lymph glands.

Of the chemical substances secreted by the ductless glands, three have thus far been separated from animals in pure form, and two of these have been synthesized in the laboratory. These two, epinephrine and thyroxin, are relatively simple bodies of extraordinary physiological potency. A solution containing one part of epinephrine in 300,000,000 will cause a marked rise in the blood pressure, when it is injected intravenously. This is a concentration of one ounce of crystalline epinephrine in about 2,000,000 gallons of solution. Pituitary tartrate extract produces a definite rise in the blood pressure in concentrations of one part in fifteen billion, which is equivalent to an ounce in 100,000,000 gallons. A mere pinch of thyroxin, administered in small portions over a year, in some cases of thyroid deficiency, makes all the difference between complete imbecility and normal health. Mind and personality are called into existence by the hormone, where there was nothing before. Yet in the face of all evidence there are still large numbers of people who firmly believe that all sorts of bodily diseases, including those connected with hormone deficiency, are subject to the control of the mind!

The ductless glands that have been noted in the human organism are present in all the lower animals, from some

Synthetic Hormones

of the lowest orders of vertebrates upward. More significant still, the hormones themselves which are produced by these ductless glands, so far as they have been studied in detail, appear to be identical in all species. The hormone, insulin, secreted by the pancreas of the ox, is suited for human use, and is apparently identical with that secreted by the human pancreas; and the hormone thyroxin, obtained from the thyroid gland of the pig, will relieve fish of the effects due to the removal of their own thyroid glands.

In the researches that have led to the discovery of these hormones, the recognition of their properties, and their final applications in medicine for the saving of human life, experimentation with animals played an important part. It was necessary to see what effects resulted from the removal of each particular ductless gland, and what effects resulted when gland extracts prepared in different ways were administered by way of mouth or by intravenous injection. Tadpoles have been metamorphosed into miniature frogs by the addition of traces of thyroxin to water. The growth of rats has been stimulated by pituitary extract, thus producing giants twice the size of their fellows. By the removal of the larger part of this gland or by the withholding of iodine from the diet, dwarfs have resulted. Female fertility in experimental animals has been diminished by administration of pituitary extract, and increased by placental extract.

In some instances, comparative anatomy and embryology have helped to establish the identity of the ductless glands of animals with particular human glands, thus enabling the functions of the latter to be studied. It has been found that certain human glands, the suprarenal glands, for example, are really two glands in one, but that these two in certain species of fish exist separately. It is possible to remove them separately from the fish and thus determine their individual functions, a feat which would

Animal
Experimentation

not be possible in animals more closely related to ourselves.

In his *New Atlantis*, written more than three hundred years ago, Francis Bacon pictured an imaginary civilization, and described in startling detail some of the experimentation with animals that is practised today, and some of the results of modern work upon the secretions of the ductless glands:

The New
Atlantis

We have also parks and enclosures of all sorts of beasts and birds, which we use not only for view or rareness, but likewise for dissection and trials, that thereby we may take light what may be wrought upon the body of man. Wherein we find many strange effects, as continuing life in them, though divers parts which you account vital be perished and taken forth; resuscitating of some that seem dead in appearance, and the like. We try, also, all poisons, and other medicines upon them, as well of chirurgery as physicks. By art, likewise, we make them greater or taller than their kind is, and, contrariwise, dwarf them, and stay their growth; we make them more fruitful and bearing than their kind is, and contrariwise, barren and not generative. . . . We have also particular pools, where we make trials upon fishes, as we have said before of beasts and birds.

THYROXIN

In the bony notch at the front of the base of the neck one may feel a small lump upon the esophagus. This is the thyroid gland. It is present in animals, from one of the lowest orders of vertebrates upward. For centuries certain serious diseases of the thyroid gland have been well known. One of them, cretinism, is very common in certain parts of the world, such as the Alps. Balzac, in his *Country Doctor*, tells of the heroic efforts of a man who spent his life among the cretins of the sequestered Alpine villages, in an effort to relieve their distressing condition. When cretinism develops in childhood, the child is stunted physically, with

Cretinism

the face and body of a little old man, and remains a complete idiot. If the disease develops later, the effects may be less serious, but are unmistakable.

Myxedema and exophthalmic goiter are also diseases of the thyroid. Cretinism and goiter occur in all races of men, in all climates. All the lower vertebrate animals may suffer from these derangements, even fresh-water fish. Most significantly, however, they have never been observed in animals that live in the sea. It was thus suggested a century ago, and later established, that goiter is due to a deficiency of iodine, for sea water contains about one part of iodine in 20 million. That trace is sufficient to protect all the inhabitants of the ocean from thyroid derangements. Iodine is a comparatively rare element, yet someone has estimated that the total weight of iodine in the ocean is about 60 billion tons.

Cretinism is a congenital thyroid deficiency occurring in children. Myxedema is exactly the same deficiency coming on in adult age. Exophthalmic goiter is an enlargement of the gland due to an excessive secretion of the thyroid hormones because of an unknown stimulus. Endemic goiter is an enlargement of the gland due to a compensatory effort on its part to make up for the body's deficiency in iodine.

Goiter has been known since ancient times in every part of the world. At one time people supposed it to be due to defects in the water supply. A generation ago, following the discoveries of Pasteur and Koch, it was often assumed to be of bacterial origin. In 1891 attempts were made to relieve goiter by the use of an extract of the thyroid gland of animals. Serious consequences followed, due as we now know to an overdosage of the powerful hormone that is contained in the thyroid gland. Then in 1895 two important discoveries were made. It was found that iodine is a normal constituent of the thyroid gland, making up about 0.2 per cent of that organ. There

are in all about 12 milligrams in the whole body, and practically all of this is in the tiny thyroid gland.

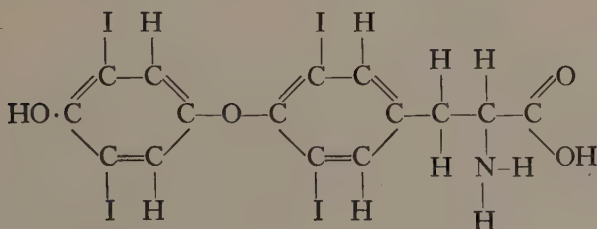
In the same year it was discovered that persons suffering with myxedema radiate heat from their bodies at only about one-half the rate of normal persons. Since the heat of the body is generated by the oxidation of glucose in the blood, it is evident that the rate of oxidation is less than normal in persons suffering from this disease. This observation made it seem very likely that the thyroid gland secretes some compound which acts as a catalyzer, enabling glucose to be oxidized in the blood more rapidly than would otherwise be possible.

In 1915 an American investigator, Dr. E. C. Kendall, of the Mayo clinic at Rochester, Minnesota, isolated a crystalline iodine compound from the thyroid gland, which he named *thyroxin*. A

Thyroxin

mere trace of this compound—less than a milligram in all—was sufficient to cause an immediate rise of the rate of metabolism, or oxidation of glucose, in a subject suffering from myxedema. The effects of a minute dose last for weeks. In one experiment, a cretinous child was given a small amount of thyroxin, amounting to only a few milligrams, administered in small portions over a period of a year. As a result, the child increased in height six inches, and developed from a condition of imbecility to normal mentality.

In 1926 the English chemist C. R. Harington succeeded in working out the structural formula of thyroxin. It was found to be an amino acid (p. 294):



The next year he synthesized this compound. Thus thyroxin, like epinephrine, may now be produced without the aid of the animal organism, and indeed in purer form than it can readily be extracted from animal tissues. Cretinism and myxedema may now be relieved and sometimes cured, and in favorable instances anatomical deformity due to goiter has disappeared under the continued administration of thyroxin.

The ancient Greeks prescribed dried sponges as a remedy for goiter. We now know that one of the amino acids composing the skeletal protein of sponges and corals is an iodine compound that differs from thyroxin only in having a hydrogen atom instead of the left-hand benzene ring in the above formula. Sponges do actually have some therapeutic value for the purpose for which the Greeks employed them. Primitive medicine pressed all manner of strange materials into service in its attempts to cure disease, and among countless failures now and then scored a success. Sponges for goiter, quinine for malaria, and chaulmoogra oil for leprosy seem to bear witness that unguided trial and failure are not altogether to be despised as a method of discovery.

EPINEPHRINE

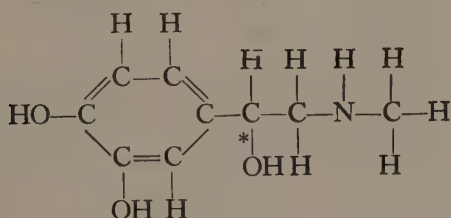
Perched on the top of each kidney is a minute body called a suprarenal capsule or adrenal gland. These glands were discovered in 1563 by an Italian anatomist, Eustachius. Each gland consists of two parts. The inner portion or cortex is traversed by great veins, which give it a greater proportionate blood supply than is received by any other organ in the body. The outer portion or medulla is entirely distinct in its cellular structure, and less plentifully supplied with blood. These two portions are in reality distinct organs, each with its separate functions.

The Adrenal Glands

In 1855 Addison's disease was first accurately studied.

It is characterized by chronic anemia, and results in such symptoms as a peculiar dingy cast to the skin and a feeble heart action. The patient gradually sinks without any sense of acute pain, and finally expires. Post mortems showed that Addison's disease was always accompanied by degeneration of the medullary cells of the adrenal glands. Thus the suspicion was aroused that the symptoms of the disease were due to failure of the diseased gland to supply some necessary hormone which was demanded for the regulation of the chemical processes of the body in a condition of health. Attempts were made to extract such a substance from the adrenal glands of animals, and these were finally successful. In 1894 it was observed that a minute quantity of such an extract produces a striking increase of the blood pressure for a brief interval of time. The substance responsible for this action we now know to be a compound of relatively simple composition, which has been named *epinephrine* or *adrenaline*. The patient's sensation of weakness is one of the most striking things in Addison's disease and suggests that an important effect of epinephrine is to maintain muscle tone.

Epinephrine was first isolated as a sulfate by Abel and Crawford, in 1897. Its composition was determined and its structural formula was finally established:



The carbon atom which is starred in this formula is an asymmetric atom, that is, it is connected with four atoms or groups of atoms which are all different from each other (p. 98). For this reason epinephrine may be optically

active. The form that is produced by synthesis in the laboratory is an optically inactive mixture of the right and left rotating forms in equal quantity. The natural product, however, is the left rotating form, which is much more powerful in its physiological effect than its optical opposite.

The content of epinephrine in the blood varies widely. It may be as little as one part in a million million, yet that small trace is quite effective in preserving the chemical balance within the body which epinephrine is intended to control. Its effects, when it is injected directly into the blood stream, are most remarkable. A mere trace causes a marked constriction of the blood vessels, including the capillary vessels, and at the same time accelerates the heart. As a result, there is a marked increase in the blood pressure. Later, however, the heart beat is slowed down and the amplitude of the beat is increased. With too large a dose, the rhythmic contraction of the heart is overcome, and sudden death ensues.

Epinephrine has a very marked effect on the rate and amplitude of respiration. Just after the injection there is a period of rest, then irregular periods of breathing, alternated with rest. In medical practice, epinephrine is best administered by subcutaneous injection. It is a means for temporary relief in threatened heart failure, and since it increases the glucose content of the blood, it is an antidote for insulin, which has the contrary effect. It relieves asthma by relaxing the bronchial muscles. Its importance in surgery is found in its action in constricting the blood vessels, thus making it useful for controlling bleeding from mucous surfaces. If epinephrine is mixed with a local anesthetic, the constriction of the blood vessels prevents the anesthetic from being carried away by the blood stream from the seat of the operation. Moreover, the area to be operated upon bleeds less freely. All this is accomplished with a quantity of the hormone which may

Effects of Epinephrine

amount to only a few hundredths of a milligram (perhaps a millionth of an ounce).

INSULIN

The pancreas is really two organs in one. It contains cells that secrete digestive enzymes; and under the microscope isolated groups of cells may be observed, which are called "Islets of Langerhans," from the microscopist who discovered them about the time of Kekulé's discovery of the benzene ring. It has been noted that persons who have died of diabetes show a degeneration of the cells that compose the islets.

The chief diabetic symptoms are an excess of glucose in the blood, and in later stages the appearance of glucose in the urine, and finally of acetone and its derivatives in the urine. The disease has generally been fatal, particularly to children. A connection between the pancreas and diabetes was indicated by the morphological changes that took place in the pancreas in diabetic subjects. The conclusion seemed to be that the pancreas secretes a hormone which controls the concentration of glucose in the blood. If the pancreas is diseased and the control fails, glucose piles up in the blood until it finally breaks down the mechanism that normally retains it within the body.

Numerous attempts were made to extract this supposed hormone from the pancreas of animals, with the hope that it would afford relief from diabetes when administered to human patients. All these attempts at first were failures. We now know that this was because the digestive enzymes in the pancreas destroy the hormone whenever the tissue is ground as a preliminary to extraction.

Success was finally attained in 1922, by Banting and Macleod at the University of Toronto, by the simple expedient of extracting the animal pancreas with alcohol instead of water. In alcohol the digestive enzymes re-

main undissolved and inactive. The hormone, on the contrary, dissolves. If the solution is then filtered, evaporated to dryness in a vacuum, and the residue redissolved in a saline solution, it may be injected intravenously in a diabetic subject. At first there were difficulties, due to impurities in the preparation. When these were finally overcome, the pancreatic extract was found to give complete relief from the symptoms of the disease. In the few years that have elapsed since this great discovery, thousands of patients have received treatment. Children who were in the last stages of diabetes in 1923 are alive today, in robust health.

The hormone existing in the Islets of Langerhans in the pancreas is appropriately named *insulin*, from the place of its origin. Its discovery after so many failures, and its present extraction on a large scale from the pancreas of animals, were favored by a number of recent achievements in experimental chemistry; for example, by electrochemical methods that make possible an accurate control of the acidity of the pancreatic extract. Moreover, the effects of the administration of insulin may be followed by a microchemical analysis of the blood. Methods have been developed by which the percentage of glucose in a single drop of blood may be accurately determined. The quantity of insulin administered may thus be accurately adjusted to the particular needs of the patient, as indicated by the glucose content of his blood. Without this safeguard there would be grave danger in the administration of the hormone. For an overdose will so far reduce the percentage of glucose in the blood as to produce convulsions. Fortunately, after such an effect is produced, instant relief is effected by injecting glucose into the blood stream.

In the case of insulin, as with other hormones and powerful drugs, the measure of the potency of solutions is commonly obtained by their effect on experimental animals. By experiments with rabbits, for example, the

strength of any insulin solution may be compared with that of a standard solution, in order that patients under treatment may be assured of a constant dosage. There is even an international standard, in charge of the League of Nations, with which the various national standards may be compared, in order that those under treatment with insulin may not run the risk of a change in dosage if they remove to distant parts of the world. The fact that all this has been accomplished since 1922 shows how quickly scientific discoveries are today reduced to practice and made the subject of international agreement. Our age is distinguished not merely for the rapidity with which new discoveries are made but for the promptness with which they are reduced to world-wide practice.

Insulin has been obtained in a pure crystalline form. Its properties show that it is chemically like the alcohol-soluble proteins. Its structural formula is not yet known, and it has not yet been synthesized. The relative complexity of the proteins makes it seem probable that its synthesis will offer difficulties. For the present, diabetic patients must depend on insulin produced from animals.

Relief from diabetic symptoms by the administration of insulin is a fair proof that the disease is caused by its deficiency. Evidence obtained with experimental animals confirms this. The removal of the entire pancreas from dogs causes diabetic symptoms. Inject insulin intravenously and the symptoms immediately disappear, but the dogs die in a few months because of the lack of the digestive enzymes furnished by the pancreas. If, however, insulin is injected and the dogs are fed pancreas daily, thus supplying both the insulin and the pancreatic enzyme, they will live on in normal health.

Unfortunately, insulin does not effect a cure. It merely relieves symptoms, if the disease has advanced so far that the tissues concerned in the production of insulin have largely degenerated. In other instances, by the injection of insulin the pancreas is relieved of its duty of regulating

the glucose in the blood, the pancreatic cells are given a chance to rest, the tissue recuperates and a cure is effected. This is the principle by which we seek to effect cures in all the group of diseases that are associated with the failure of ductless glands to perform their normal functions.

THE SEX HORMONES

The hormones secreted by the gonads or sex glands, like other internal secretions, influence growth and determine character and behavior as well as bodily shape. Nevertheless, the prime purpose of the sex hormones is reproduction, while the other endocrine secretions operate for the benefit of the individual without regard to the preservation of the race. A great deal of work has been done with the sex hormones, and some very remarkable facts have been discovered. It has been noted that the secondary male characteristics of fowls, such as the color of plumage and the development of the comb, are determined by the male hormone. If the female hormone is administered to young cocks, the secondary female characteristics appear. At this level in the evolutionary scale of animals, the secondary characteristics of either sex may be brought uppermost by administration of the proper sex hormone. Among mammals, however, each individual seems to be definitely sexed, and reversals in secondary sexual characteristics as a result of the administration of hormones of the opposite sex have not been observed.

The male hormone is believed not to vary in its chemical identity even when derived from widely different species of animals. Thus serums from young bulls and stallions, when administered to senile or castrated cocks, cause a return of masculine characteristics. The action of the male hormone or hormones is, moreover, not inhibited by administration by way of mouth. Other

hormones, by contrast, often need to be administered intravenously or intramuscularly.

Attempts to rejuvenate animals by gland transplantation or by the injection of hormones, have never led to any permanent result. In fact, it has not been established that senility is the result of a failure of sex secretion or a loss of sex hormone efficiency. It seems very possible that unknown, deep-lying causes bring about a general decline of the bodily organism in old age, of which the decline of fertility is but an incidental part.

Some very remarkable results are being obtained in studies of female fertility as determined by diet or the administration of hormones. The ovarian hormone greatly shortens the menstrual cycle in female animals, while corpus luteum extract lengthens the cycle and delays ovulation; and since fertility is dependent on ovulation, means are thus afforded for controlling fertility. Investigations are being very actively carried forward, and the application of this knowledge in the control of the fertility of domestic animals may perhaps be near at hand.

Though such progress is encouraging, we must admit that the chemical nature of the sex hormones is completely unknown. The manner in which they influence other organs of the body or cause the development of secondary sexual characteristics is still undetermined. Extracts from the animal glands that have thus far been employed have all been unstandardized preparations, and have generally been ineffective. The quest of the Fountain of Eternal Youth is not much more promising today than it was in the time of Ponce de Leon.

We have said enough to indicate that our state of health and activity is very intimately connected with the presence in the blood stream of mere traces of substances which we have only recently identified. There may be dozens of others, yet

Conclusion

undiscovered, the presence or absence of which, or surplus or deficiency, determine health, character, and personality. Not only mechanically, but chemically, we are fearfully and wonderfully made.

Does fate seem too inescapable when thus identified with our chemical heredity? No more than it did when it was linked with heredity of an unspecified sort. We have long known that the sins—and the virtues, too—of the fathers are apt to be visited on the children to the third and fourth generation. Yet the knowledge that our chemical inheritance may be better or worse than another's can not relieve us of the duty of doing what we can with the portion that comes our way.

The physiological chemist, by his contributions to our understanding of the chemistry of the internal secretions, is giving the human race some new responsibilities and problems. For the first time since life appeared on the earth, an animal species will perhaps come into the biochemical control of its own rate of reproduction. For the first time, all sorts of defects in heredity will temporarily be made good, thus enabling the weaker members of the race to reach maturity and perpetuate their weakness in succeeding generations. More and more, the fit and the unfit, the noble and the ignoble, the worthy and the unworthy, will live on together past the age of productive effort, to become an economic burden for the younger generation.

Yet the loss by this should be more than offset by the gain that the finer spirits among mankind, whose lives mean something in human life, will have their years of usefulness prolonged. Robert Louis Stevenson said: To remain alert to all the bright contacts of human experience; to plan splendidly, and press forward, flushed with hope, to the very end—"surely, at whatever age it overtake the man, this is to die young. Death has not been suffered to take so much as an illusion from his heart. In the hot-fit of life, a-tiptoe on the highest point of being,

he passes at a bound to the other side. The noise of the mallet and chisel is scarcely quenched, the trumpets are hardly done blowing, when, trailing with him clouds of glory, this happy-starred, full-blooded spirit shoots into the spiritual land." This describes a happy chemical inheritance.

CHAPTER XXIV

LOOKING TOWARD THE FUTURE

THE achievements of the recent past very often indicate the nature of those of the near future. To that extent, it is safe to prophesy. For the more distant future a prophecy is just an expression of hope, since the direction of progress in any field is likely to be altered at any moment by some fundamental new discovery. Still, let us look forward.

A New Point of View

Organic chemical research in our universities has often seemed to be conducted for the sake of the naïve satisfaction that was found in the creation of compounds never made before. Whether the substances thus produced were likely to be useful, or whether the methods of their preparation threw any light on structure or suggested new methods of synthesis was often a matter of indifference. Research of this kind is becoming more rare. Organic chemistry has passed from the systematizing period, in which attention was chiefly directed to classifying compounds and filling in the gaps in existing classes. We have ceased to be greatly troubled that a few of the theoretically possible isomers of a given substance have not yet been discovered. In the immediate future the effort will rather be to determine in detail just how chemical changes are accomplished, and what the conditions are for carrying out each type of change most readily and completely.

We understand today that the atoms of our chemical elements are not solid, indestructible structures, but are

complex aggregates of positive and negative electricity.

**Electrical
Forces
between
Atoms**

We even know something of the manner in which these electrical charges, the protons and electrons, are disposed with respect to each other in building up the atom. Yet, up to the present moment, no noteworthy application of these new discoveries has been made in the field of organic chemistry.

We still speak of the atoms as being linked together within molecules in a purely mechanical way, by connecting strokes or valence bonds. We know better. We understand well enough that atoms are drawn together by electrical forces; yet we still speak of chlorine and hydrogen as becoming attached at double and triple bonds, in the very language that was used by the organic chemists of more than half a century ago. What the process is in terms of electrons we have not yet really visualized.

Presently all this will be changed. Our structural formulas will suddenly become more complex, due to the introduction of symbols intended to express the electrical configurations of molecules. Yet, to the initiated, these symbols will bring increased simplicity. The chemist, in synthesizing new compounds, will be able to see more clearly than he can with the aid of our present formulas just what sort of reactions are possible for a given substance. He will no longer work by rule-of-thumb methods that direct him to heat the mixture on a water bath under a reflux condenser for seven hours. If these are really the right conditions of concentration, temperature, time and pressure for producing the desired result, he will know why.

No one can help being impressed by the fact that the most important triumphs in chemical synthesis during recent years have been those accomplished with the aid of catalyzers. Yet the mode of action of most of these has escaped us. We know that some of them act by combining temporarily with other

Catalysis

substances to form intermediate products. Others act by condensing the chemical reactants on the catalytic surface, thus bringing the reactants into intimate contact with each other. That many reactions are accomplished entirely at the surface of the catalyzer is evidenced by the fact that the activity of such catalyzers as nickel, platinum and charcoal is increased in proportion to their surfaces, as the material is more and more finely divided.

Yet this is but the beginning of knowledge. The future should enable us to understand just what happens in particular cases. The experiments of Langmuir, in recent years, on the reactions that take place at high temperatures at the surface of a tungsten filament under very low pressures, are examples of the sort of investigations that will need to be carried out to determine the nature of the action of surface catalyzers. The chemist of the future will have a picture in his mind's eye of the relationship of the atoms in the surface of the catalyzer to one another and to the atoms of the substances which are condensed on that surface as a preliminary to their interaction with one another.

The remarkable catalytic effects of enzymes and hormones in nature suggest possible applications in the chemical laboratory. Already some studies have been made of thyroxin as a catalytic agent. The hormones thus far synthesized are of such comparatively simple structure as to encourage the hope that we may presently discover means for producing substances of no greater complexity, to serve as catalyzers in reactions carried out on an industrial scale.

Current progress in theoretical chemistry will have a profound effect on organic synthesis. Thermodynamics, the science which deals with the principles that govern transformations of energy, will intervene at the very beginning of certain experiments with the remark, "The laws of energy show this reaction to be impossible"; but will lend encouragement to others

Energetics

by saying, "Here is something that theoretically should be possible, but has never yet been done. Let's find a way to do it."

The trend of the times is to bring about the union of gaseous materials in the presence of catalyzers at pressures of several hundred atmospheres. Yet these are trifling pressures in comparison with those that existed in the depths of the earth when natural gas and petroleum were formed. If we are to understand how these materials came into existence, and if we are fully to exploit the chemical possibilities of coal as a raw material for the synthesis of liquid fuels and other products, the pressures must go higher.

To effect such transformations on a commercial scale will call for new engineering developments. The engineer has made syntheses possible that chemistry alone could not have effected. In return, chemistry has furnished engineering with its most useful materials. The demands of technical chemistry will lead to new achievements in engineering. Rubber-lined metallic tanks are now becoming common. Glass pipe of a sort that resists sudden temperature changes is being used to convey corrosive liquids. Alloys have been developed to resist high pressures and to withstand corrosion or retain hydrogen at high temperatures. Synthetic resins are coming more and more into use as engineering materials.

The chemist of the future will make more effective use of electrical processes than is now done. Oxidation and reduction are only matters of abstracting or adding electrons, and are thus most directly accomplished by the electric current. More and more, reactions will be used in which molecules are activated by electrical discharges or by the action of ultra-violet light.

Purely chemical methods of investigation, inherited from the days of Berzelius and Liebig, will more and more be replaced by physical instruments and methods.

Electrical
Processes

X-rays will soon be in familiar use, as an aid in identifying substances, even in the organic laboratory. Optical instruments of all sorts will be developed far beyond their present state, and optical principles still undiscovered will direct visible and invisible light toward a multitude of new uses in furthering research. The existing barriers between physics and chemistry will be largely broken down. Measurements of electrical and electromagnetic properties will be matters of familiar routine, as an aid to organic research. Sources of intense energy, now known or unfamiliar, and physical apparatus still to be devised, will enable us to interfere, more directly than is now possible, with the electrical events that accompany and determine the course of chemical changes.

A survey of recent progress in chemical synthesis leaves a vivid impression that the most striking current achieve-

**New
Industrial
Products**

ments are being made in the aliphatic field: acetylene and its numerous derivatives, glycerol and glycol, urea and thiourea, alcohols, esters, fatty acids, rubber, carbo-

hydrates—here is a vast field still open to exploration, with synthetic possibilities surpassing any that have yet been realized. In the past, attention for a long time was chiefly devoted to the ring compounds, and these were developed and exploited disproportionately.

In consequence of synthetic progress, new industrial products will come into being. Each decade will enrich our lives with numerous new materials. The lexicographers will be hard put to it to record and catalogue the new words which will enter our language as by-products of the activities of the synthetic chemists. Cellulose derivatives of all sorts will play a part in our daily lives quite surpassing that played today by rayon or by cellulose nitrate or acetate. It is inconceivable that the nitrate and acetate should be the only esters of cellulose worthy of careful study or commercial exploitation. Lacquers will be produced with more flexibility and greater resist-

ance to the destructive action of sunlight or ozone than any now known.

Synthetic rubber and rubber-like substances are apt very soon to enter the market. The raw material that stands most evidently at hand for their production is natural gas. It seems a pity that so marvelous a raw material should be largely devoted to the production of carbon black, by a process of incomplete combustion, with a yield of carbon of only a few per cent.

Far wider use will be made of plastic materials. There are whole classes of compounds, practically uninvestigated, that might be expected to react with each other in a manner to give plastic resinous products. Throughout the fields of industry, the substances which have been developed and put into widest use are frequently those which were first noted as being suitable for the given purposes. A careful survey of related compounds should often result in a discovery of other substances, better suited to each given purpose than any now in use.

Time was, when chemical synthesis aimed at duplicating compounds already known in nature. Next it sought

Molecules
Made to
Order

to produce acceptable substitutes for these compounds. In the future we shall more generally realize an ideal that has inspired recent researches in the synthesis of local anesthetics: To take note of the properties which the practical ends in view demand that the compound to be synthesized shall possess; to infer what molecular structure will confer these properties; and then to build that structure. Thus many useful substances quite unlike any ever known in nature will come into common use. In so producing molecules "made to order," possessing properties specified in advance, the chemical mode of thought will have won an impressive triumph.

Increased knowledge of general principles will enable us to build with speed and confidence, from simple to complex molecules. Even colloidal substances, such as

starch and the simpler proteins, will perhaps be readily elaborated. Many new classes of organic compounds will be discovered and hundreds of thousands of compounds will be added to classes already known. Yet the study of organic chemistry will not be made more difficult by this great increase in the mere number of chemical compounds, for there will be a striking increase in orderliness. We shall doubtless learn to duplicate many of the reactions by which green plants synthesize complex organic compounds at the expense of the energy of sunlight. Yet this is far from predicting that it will ever be economical to displace green plants by chemical apparatus, as a means for producing any important part of our food.

Developments are in sight in which micro-organisms will doubtless be put to work on a large scale to effect chemical changes of many kinds. The commercial fixation of atmospheric nitrogen by bacteria with the direct production of useful nitrogen compounds will perhaps be realized in the near future. Means may be found to reduce the great quantities of straw, cornstalks, cotton stalks and other agricultural wastes—estimated to be at least a billion tons a year in the United States alone—to simple and useful compounds by controlled fermentation.

In the Orient, molds have long played an important part in the alteration of food materials, such as the soya bean, into more readily digestible or more palatable forms. In Europe and America their use has been practically limited to giving flavor to cheese. The future will doubtless see much more important industrial exploitation of their chemical activities in the transformation of food-stuffs.

Yeasts, too, will doubtless become important articles of food, not merely because of their high content of vitamins and important phosphorus compounds, but because they are able to convert the nitrogen of ammonium salts into proteins, at the expense of the energy

Setting Micro-organisms to Work

Proteins from Yeasts

stored in sugar. Yeasts need no sunlight because they make use of sunlight that fell on green leaves in cane or beet fields in some former growing season. Sugar is over-produced. The sugar-growing regions of the world compete against each other, dump millions of tons of surplus production on markets already glutted, and depress prices to the point of no profits. What more logical solution to the economic problem thus presented than to feed sugar to yeasts and molds, thus securing protein foods whose equivalent could otherwise be secured only in a far less economical way by devoting great areas to foraging or to grain crops for feeding animals.

If developments such as these are presently realized, they will doubtless be hailed as chemical triumphs. Yet again, as in so many organic industries, chemists will do little more than control, protect and advise. Engineers will furnish the micro-organisms with a happy environment, and the micro-organisms themselves will do the work. The opportunity for chemical service will be in discovering how the micro-organisms accomplish these changes in order that they may be duplicated without the aid of micro-organisms. To accomplish this we shall probably need to discover much that is still unknown concerning the nature and mode of action of enzymes.

Progress in chemical synthesis in the immediate future should bring forth new marvels in physiological chemistry.

Physiological Chemistry The separation and synthesis of the vitamins will perhaps not be long delayed.

We shall then have complete control over some common diseases due to defects of nutrition. One by one, the digestive enzymes will be synthesized, and the chemical regulators of personality. When individual organs fail to perform their proper chemical functions, we shall be able to step in with synthetic hormones and keep the bodily mechanism running while we seek to effect a cure.

We shall have new methods for experimenting with individual living cells, to determine the reactions of pro-

toplasm of different types toward chemical influences of all sorts. In consequence, we shall be able to proceed more intelligently, in efforts to destroy bacteria and protozoa within our own bodies without risk to the bodily cells. Synthetic medicines will be our chief reliance in our warfare against disease. Some of the principal ills that now beset mankind will be banished utterly.

We shall understand more of what goes on when cells grow and subdivide, producing new tissue. We shall have new methods for studying isolated organs, in continued vital activity, outside of the animal body. The results will do much to inform us concerning the chemical work that each organ does, the chemical environment with which it should be surrounded, and the alterations that it experiences, in disease or old age.

These new discoveries will be put to immediate use in surgery and medicine. The transplantation of organs will become commonplace. Time-honored palliative remedies will be displaced by cures. More and more we shall learn how to maintain our bodily cells in that happy chemical state which we call youth. We shall not merely add to the span of life, but shall make life more worth living.

Yet our sense of satisfaction that such progress will be the means of prolonging many lives is diminished by the thought that chemical science cannot promise that all of them will be worth prolonging. It is pleasant to toy with the fancy that synthetic chemistry may some day produce a spiritualizing or social-impulse-stimulating hormone of such potency that a few milligrams, administered intravenously, shall be able to convert a self-centered, grasping miser into a philanthropist.

No great prophetic gift is needed to foresee that the chemical progress of the immediate future will compel progress in chemical education. It will be realized that scientific instruction is not a bit more scientific when dry as dust. On the contrary, it will be understood that the teacher who

**Chemical
Education**

presents scientific facts without any attempt to relate them to the philosophy of science or to human life is one who has failed to think about them. He gives only facts because he has only facts to give.

In the future, there will be the utmost diversity in the choice of topics for instruction, and in the order and modes of their presentation, in a constant attempt to discover better methods of stimulating thought. Chemistry is an experimental science. The days of standardized courses and standard lists of topics will be over, for it will be realized that the student is not a vessel to be filled, but a fire to be kindled. The textbooks of the future will not consider it aside from their duty to point out the economic, social, political and moral implications of scientific facts, for we shall have a better understanding of what education is for, and a clearer vision of the part that chemistry is fitted to play in furthering the ideals of citizenship. Chemistry as a science will constantly become more mathematical, technical, and forbidding; yet chemistry as a cultural subject will ever be more attractively presented, more useful as a part of a general education, and more intimately related to other things worth while.

Discoveries in the Realm of Carbon are but a part of the great advance that is being made in all the fields of science. We need not peer very far into the future to discover an age in which all the material comforts that may cheer, enrich and bless human lives will be available to a larger proportion of the earth's inhabitants than ever before. Means will be found to insure that humanity at large shall more generally enjoy the opportunities that material progress should offer to all for leisure, joy and self-development.

It stands to our disgrace that with all our science we have developed no higher social state than one that permits the resources of the earth to be exploited so waste-

fully by the present generation, without regard to the needs of the future; and one in which a few possess material comforts so far in excess of their capacity for enjoyment, while multitudes lead lives that are never free from hardship, toil and anxiety. To what end is Nature subdued but that Mankind may be free? Science has lightened the tasks of our hands that our spirits may attain the heights.

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